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ENERGETIC MATERIALS HAZARD INITIATION:

DoD ASSESSMENT TEAM FINAL REPORT

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Technical Editors
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PREFACE

The intent in assembling the present overview of energetic materials hazard initiation was to obtain continued participation as well as written contributions from DoD experts in the various technical areas. Members of EMHIAT who have co-authored the various sections of this report are identified below; other members were equally essential in various phases of the activity and are listed in the Acknowledgements. As Technical Editors, we express our appreciation to each individual who served for his/her valuable time, enthusiasm, and commitment.

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AMM acknowledges support from the Army Research Office under Intergovernmental Personnel Agreements for both academic years 1985-86 and 1986-87 and the technical challenges offered by Drs. Robert E. Singleton and David M. Mann of the Engineering Sciences Division, who made organization of EMHIAT worthwhile and stimulating. Further, he thanks Marie Sander and Jacqueline Gilmore of ARU for typing the manuscript with care and patience, and Steven J. Ritchie of Drexel University who prepared the figures and provided support in innumerable other ways.



ABSTRACT

The Army, Navy, and Air Force Energetic Materials Hazard Initiation Assessment Team (EMHIAT) was established in late 1985 to identify basic and applied research needs to mitigate hazards, particularly for solid rocket propellants, represented by unplanned initiation in manufacturing or handling fielded systems and during processing of energetic materials. The team has surveyed the solid rocket industry, the DoE contractor laboratories, and DoD efforts related to explosives, gun, and rocket propellants. Findings of the survey and a Long-range Plan for Hazards are summarized in the present report.

In July 1986 the DoD Joint Requirements Oversight Council issued criteria for Insensitive Munitions, all of which contain energetic materials. EMHIAT strongly recommends the Plan documented here as essential to meeting these criteria in a cost effective and timely fashion.



CHAPTER I. INTRODUCTION AND SUMMARY

High explosives, pyrotechnics, gun propellants, and rocket propellants represent the potential for catastrophic accidents in the case of inadvertent ignition or initiation. The design of low vulnerability energetic materials is one aspect of the Insensitive Munitions Program which the Department of Defense is now emphasizing (JROC, 1986). Although this aspect of hazards reduction primarily involves fielded systems and the user community, mitigation of processing and manufacturing risks is of equal importance to industry. A Tri-Service team was established in November 1985 to assess current hazard technology and to develop a research plan to correct deficiencies identified in the assessment (Mellor, 1986). This Tri-Service group is called the Energetic Material Hazard Initiation Assessment Team (EMHIAT). Although the initial emphasis of EMHIAT is solid propellant rockets, Department of Defense representation includes both the explosives and propellant communities through laboratories from the Army, Navy and Air Force, as well as the appropriate 6.1 organizations.

In the past funding limitations have largely curtailed hazards work in the rocket industry to that required by a specific contract (Flanigan et al., 1986), a specific fielded system, or an incident (Hermesen et al., 1986). The situation is compounded by the existing hazard test methods: both industry and the user community find these neither meaningful nor realistic, frequently misleading in terms of accident potential or ease of initiation in a practical scenario, and not useful for fielded system risk analysis (Hermesen et al., 1986; DeButts et al., 1986; Flanigan et al., 1986; Weiss et al., 1984). The Air Force has identified poor communication between designers and those

scientists and engineers performing basic hazards research as an additional concern (Weiss et al., 1984).

EMHIAT has been formed at the present time due to both the above problems and a number of incidents in each of the services. The costliest and most expensive in terms of human life involve aircraft carrier fires in the Navy (Boggs et al., 1985). In addition, the Pershing II incident in Germany in 1985 (Anon., 1985a) and accidents involving catocene additives in production facilities (Roberto, 1986) have caused much concern in the other two services. As a result, each service has established an energetic material hazards program, in which threats to fielded systems are considered. These threats include sympathetic detonation, fast or slow cookoff, single and multiple bullet or fragment impact(s), electrostatic discharge, and electromagnetic radiation.

By choice, however, the focus of EMHIAT is the underlying hazards technology base resulting from the fielded system threats listed above. These 6.1 and 6.2 areas identified by EMHIAT include: critical or failure diameter; shock to detonation transition (SDT); deflagration to detonation transition (DDT); delayed detonation (XDT); thermal response and ignition; friction; impact; and electrostatic discharge (ESD). Combinations of the last four initiation stimuli are also of particular interest. Although toxicity is another important concern (DeButts et al., 1986), it was not included in the present study.

There is usually a trade-off between maintained or improved performance and decreased hazard sensitivity, but an increased research effort in both

formulation and hazards characterization could identify exceptions. The weaker area here is the latter since quantitative information and parametric studies are often lacking when current hazards tests are utilized. Thus the objective of EMHIAT is to establish via a state-of-the-art assessment what research and technology needs will assist in mitigating hazards associated with energetic materials. Part of the approach EMHIAT has used is to distribute a questionnaire package to selected industry and contractor laboratories, who responded in April 1986 with oral briefings to EMHIAT, as well as with written reports in some cases. EMHIAT has reviewed all of the information obtained and prepared the present summary report and long range research and technology plan involving each of the technical areas identified above. This overall procedure has provided direct input to EMHIAT from those most concerned with energetic material hazard initiation for solid propellant rockets. Further, the technology organization is consistent with NATO Action Committee 310, concerned with suitability of service and safety of munitions (see for example Brace, 1984).

The questionnaire utilized is reproduced in Appendix A. The respondents were requested to itemize their small and large scale test methodology, to explain deficiencies of the test procedures, test results, and applicability to the relevant fielded system threat, and then to discuss their perceptions of basic and applied research needs in that technical area. The method of initiation, propellant formulation, geometry, age/damage, initial temperature, humidity, and confinement were specifically called for in the questionnaire, as well as any parametric study results for these latter variables.

The organizations which have participated in the EMHIAT assessment include, from industry, Aerojet, Atlantic Research Corporation, Chemical Systems Division of United Technologies, Hercules, Morton Thiokol, Rocketdyne, and Talley Industries. In addition, Lawrence Livermore National Laboratory, Los Alamos National Laboratory, and Sandia Laboratories responded. DoD expertise has been utilized through the written contributions to the present summary report, as discussed in the Preface, and through critical readings of early drafts, as listed in the Acknowledgements. Major findings are summarized below.

In terms of mechanistic understanding, critical diameter, shock to detonation transition, and thermal response and ignition tend to be the more mature of the eight technology areas considered in the questionnaire, whereas electrostatic discharge is undoubtedly the least. The existing traditional energetic material hazard test methods, to be discussed in the next chapter, are in general inadequate to rectify the situation because, as will be demonstrated in the remainder of the report, they are too ill-defined in terms of first energy input with time, second diagnostics from time zero to ignition, third, interpretation of the initiation itself, and fourth, modeling on a fundamental level. Consequently there are few meaningful parametric datum bases.

Thus the design and fielding of munitions (containing energetic materials) which are insensitive to unplanned stimuli will require an expensive and time-consuming cut-and-try approach. The Long-range Plan offered at the conclusion of the report identifies research opportunities for explosives, rocket, and gun propellant hazard mitigation. Although little of

this work appears to be ongoing in or funded by the appropriate DoD agencies, EMHIAT concludes that the Plan presents urgent technology needs if the Insensitive Munitions are to be available on a timely and cost effective schedule.

In Chapter II current test methods, typical test results, and selected parametric studies are reviewed for each technical area. Deficiencies in understanding, both for each technical area and in a more fundamental vein are identified in Chapter III. The resulting near and far term technology needs are discussed in the following chapter, and the report concludes with the Long-range Plan on Hazards in Chapter V. This Plan contains elements for industry, government laboratories, and universities having the personnel and skills necessary to contribute in this research effort.

Because 6.1 research needs are included, EMHIAT is somewhat more university oriented than the JANNAF Propulsion Systems Hazards Subcommittee, although both have fully consistent goals and efforts. Further, the EMHIAT technical organization is compatible with that of NATO AC/310 and therefore provides direct input to the proposed AC/310 Information Center. All of these complementary activities should assist in bringing energetic material hazard mitigation to its proper position in the design process for munitions.

CHAPTER II. HAZARD TESTS - PRACTICE AND DEFICIENCIES

A. Critical Diameter

The critical diameter (d_c) is defined for cylindrical, solid energetic materials as the minimum diameter at which a steady state detonation can propagate (Price, 1981). As such, the concept of critical diameter is an important one for the relation of the inherent hazard of the energetic material to the vulnerability of the system incorporating the material. The critical diameter of energetic materials is known to be a function of composition, particle size, porosity, temperature, confinement and shock initiation pressure. Fairly recent reviews of the interrelationships of these factors are available in the literature for explosives (Price, 1981) and high energy rocket propellants (Gibson, 1986). Particularly for diameters greater than d_c , there is a strong variation with shock initiation pressure. For determination of d_c , initiator charges are selected such that the shock pressure is well above critical, threshold values.

The definition of critical diameter virtually determines the requirements for any test: i.e., samples of successively larger diameters are tested until one is found for which a detonation propagates. All tests for d_c incorporate the same basic procedure: initiation by a suitable donor charge and determination of steady-state detonation from examination of witness plate, photographic or probe records. Since, for most energetic materials, and particularly for explosives, the critical diameter is on the order of millimeters to centimeters, the tests can generally be classified as "small scale," and most of the d_c data has been generated using these tests. However, rocket

propellants, at least before the advent of high-energy, HMX/RDX formulations, generally have critical diameters of tens to hundreds of centimeters. Not unexpectedly, there are little data for such large scales.

1. Small Scale Tests

The simplest and most straightforward of the d_c test methods is the individual testing of cylinders of varying diameters. To ensure adequate distance for the development of a steady-state detonation, length-to-diameter ratios of 4 to 10 are typically used. Since the testing of many samples can be a slow and expensive process, novel test procedures have been developed to obtain the data in a single firing. By machining the material into a tapered wedge, cone or stepped cylinder, a single test can be used to determine d_c from the material thickness at which a detonation is no longer propagated (cf. Jaffe and Price, 1962; Dobratz, 1981). Data from the wedge and conical geometries must be corrected for the overdriving of the detonation from propagating into non-propagating regions. This is done by varying the wedge or cone angle and extrapolating to zero angle. Since d_c is defined for a cylindrical geometry, it is also necessary to correct wedge or square cross section data to an equivalent, circular d_c . Semi-empirical correction factors, determined from extensive testing of composite rocket propellants (Elwell et al., 1967) are frequently used.

2. Large Scale Tests

Composite rocket propellants, typified by formulations of Al/AP/binder, can have critical diameters of tens of centimeters. Project SOPHY (Elwell et al., 1967), conducted by the AFRPL in the '60s, was a landmark in the

characterization of the hazards associated with energetic materials having large d_c . Under this program, the properties of the composite propellant ANB-3226, 69% AP/15% Al/16% PBAN binder, were extensively analyzed. The predicted d_c for this propellant was found to be 163 cm (64 in). This prediction was tested using firings of 152 cm (60 in) and 183 cm (72 in) diameter cylinders of propellant. The 183 cm test configuration was a 12.8 m (42 ft) high stack consisting of 5.5 m (18 ft) of TNT booster on top of 7.3 m (24 ft) of propellant. The booster weight was estimated at 8,200 kg (18,000 lb) while the propellant weight was estimated at 33,600 kg (74,000 lb). Test results verified the prediction but also underscored the difficulties associated with instrumenting and controlling such a large test. Studies were also conducted to determine alternative methods to such full scale testing. Sensitizing the propellant by replacing some of the AP by RDX was demonstrated to be a reasonable means to determine d_c by extrapolation of results for sensitized mixtures to zero RDX content. Figure 1 shows the behavior of d_c with RDX concentration. While not exactly reducing the problem to small scale, the method appears attractive.

3. Selected Results

Figure 2 (from Price, 1981) illustrates the two types of behavior observed in d_c data. The so-called Group 1 materials, TNT and other of the more powerful organic explosives, exhibit a decrease in d_c as they approach maximum density. The Group 2 materials, AP, AN, AP+fuel, etc., show an increase in d_c with increasing density. This differing behavior has been attributed to the dominance of homogeneous reactions in Group 1 materials and a dominance of

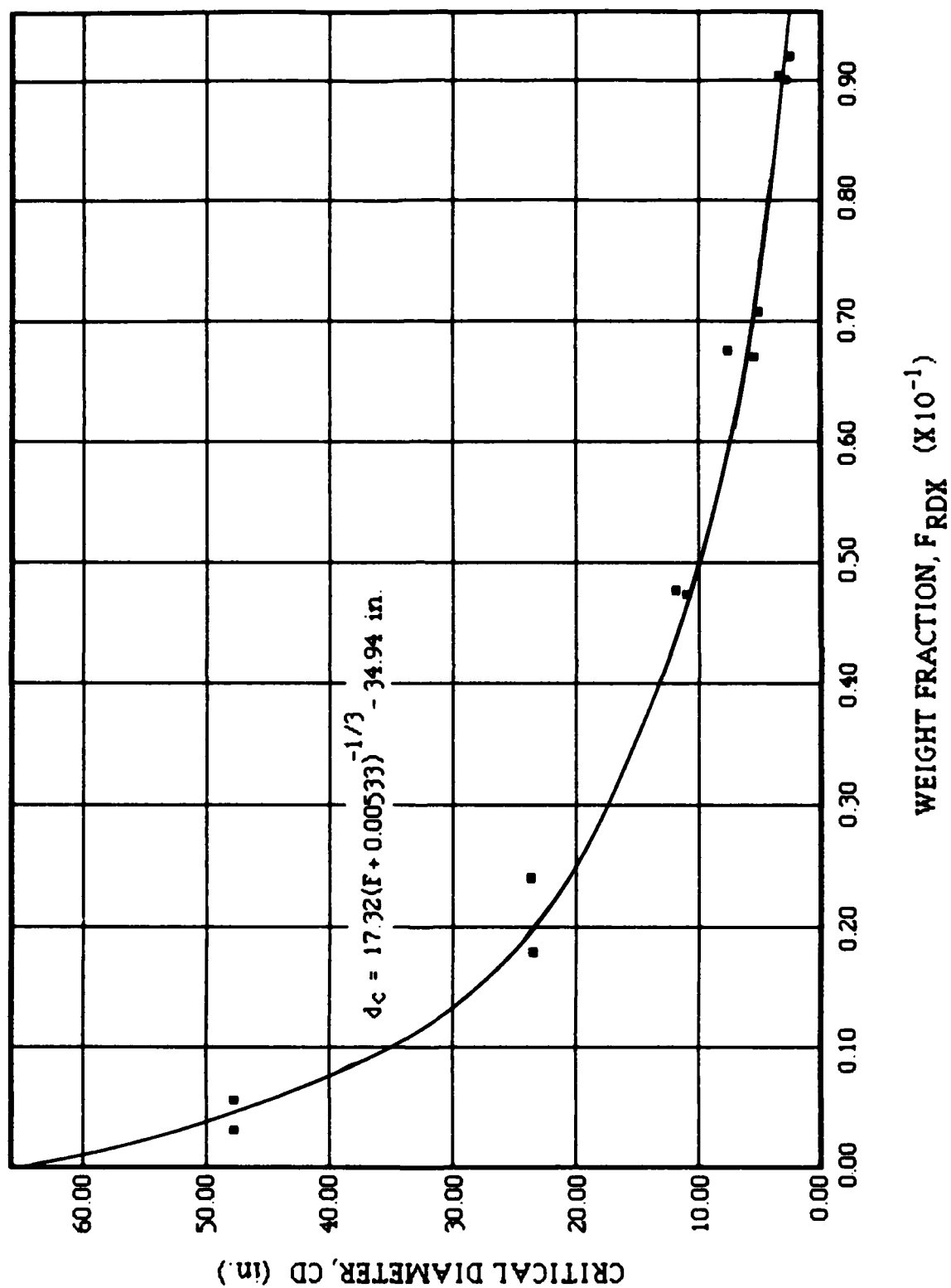


Figure 1. Detonation model for ANB-3226 propellant adulterated with RDX (from Elwell et al., 1967)

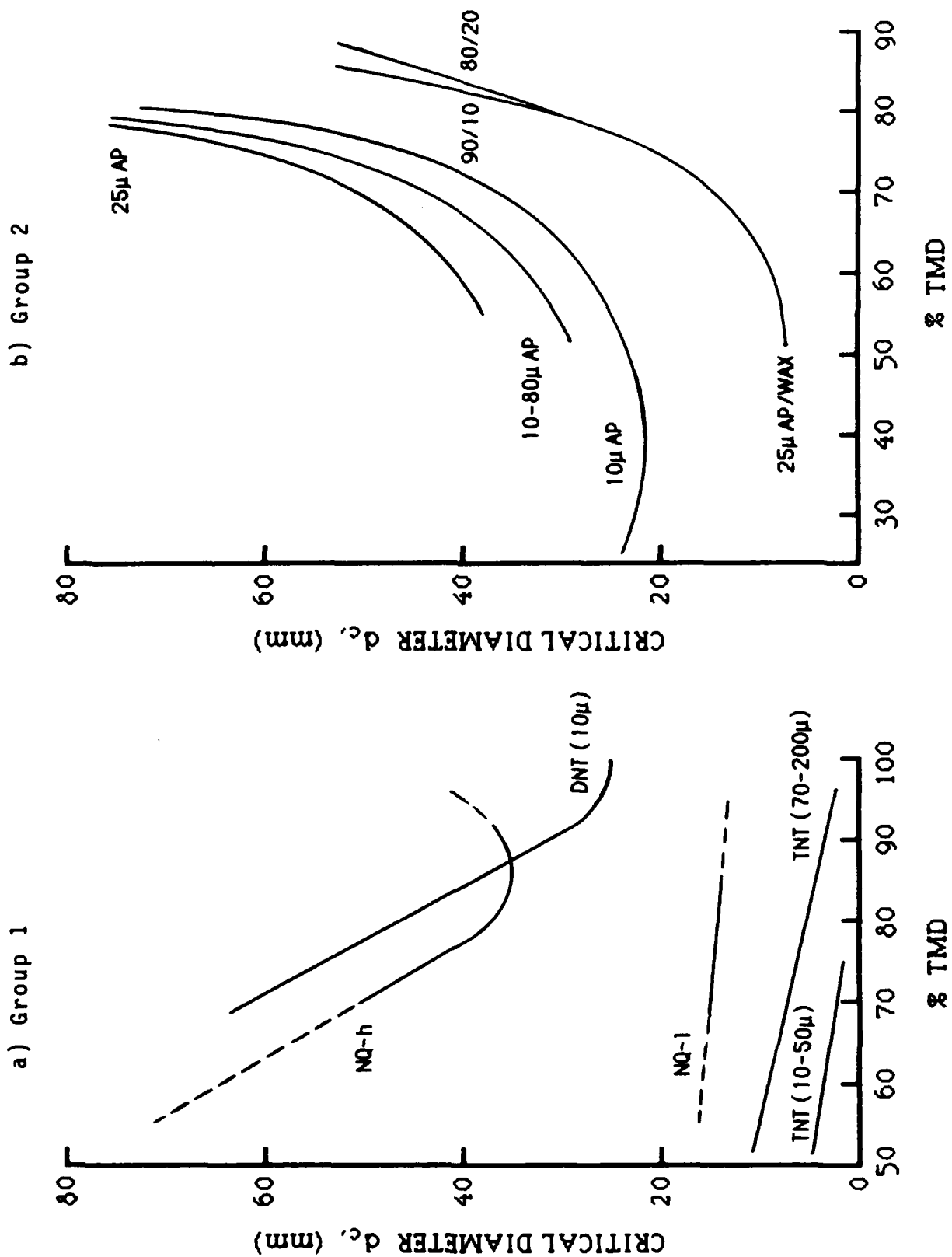


Figure 2. Detonability curves (from Price, 1981).

surface, or heterogeneous reactions in Group 2 (Zerilli, 1981). Mixtures of the two material types exhibit intermediate behavior with a smooth transition as a function of composition, as illustrated in Figure 3 for AP/HMX mixtures (Akimova and Stesik, 1976).

4. Parametric Studies

The relatively high shock sensitivity and resultant small critical diameters of explosives have made them the obvious candidates for extensive, parametric studies. Figures 2 and 3 are representative of the studies which have been conducted. Many more are available in the literature (cf. Price, 1981 and references therein). With the advent of high energy formulations, some parametric studies of rocket propellants are also available (cf. Gibson, 1986). However much of these data have not yet appeared in the literature.

B. Shock to Detonation Transition (SDT)

The discussion of shock-to-detonation transition (SDT) presented here is not intended to be exhaustive. Rather, it is in the way of a brief overview. Further, it is intended to distinguish SDT from its close and distant cousins, deflagration-to-detonation (DDT) and unknown-to-detonation (XDT) transitions.

To begin with, we will use as a definition of detonation a coupled supersonic wave system consisting of a compression shock and steady zone of reaction which drives the system. The shock is a pressure and density discontinuity driven by the exothermic chemical reaction. The pressures and times necessary to initiate reaction are typically a few tens of kilobars pressure and time durations of a few microseconds (see Zerilli, 1981, p. 98). The response of an explosive varies somewhat with the nature of the shock.

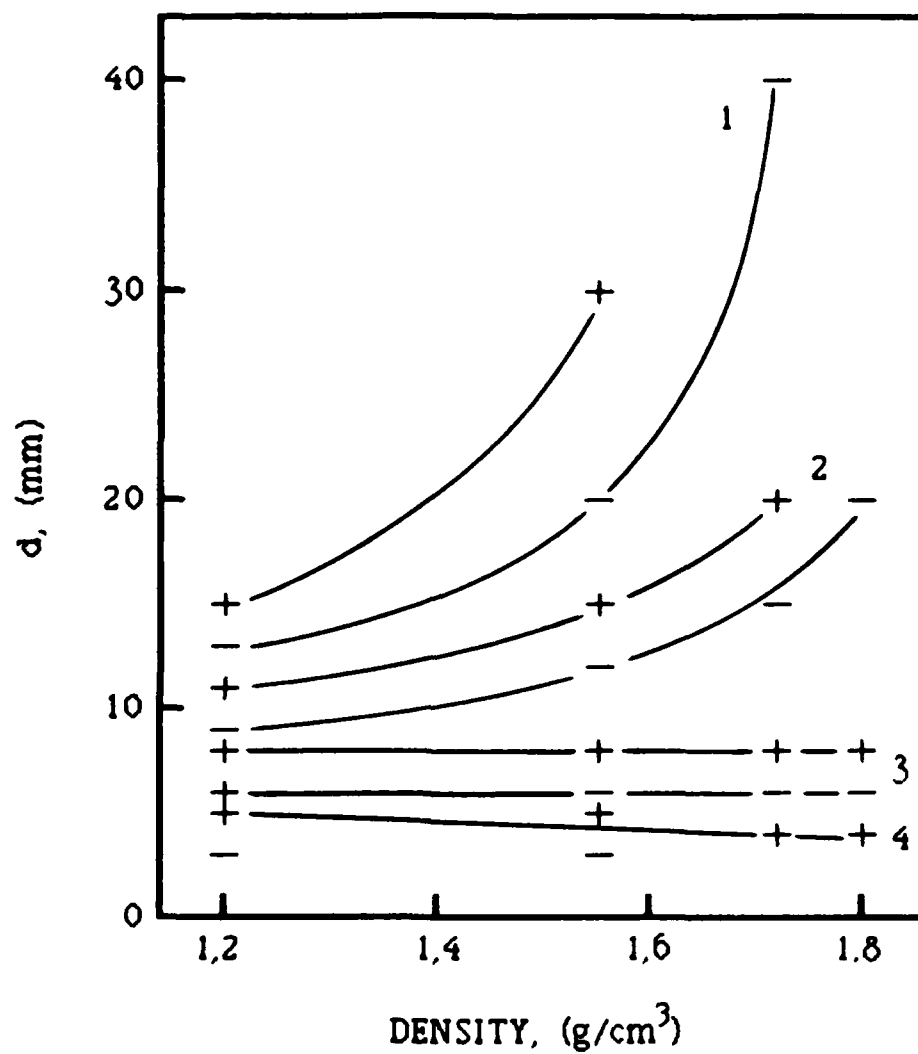


Figure 3. Density dependence of d_c for AP mixed with HMX: 1) 95:5; 2) 90:10; 3) 85:15; 4) 75:25 (from Akimova and Stesik, 1976)

Ramped shocks, sustained pulse shocks and thin pulse ones all give rise to somewhat different responses. See Starkenberg et al., 1985 for an example of the effect of different shock pulse shapes on the initiation of cased explosives. Many common explosives exhibit thresholds for detonation to square pulse shocks governed by some relation of the form

$$P^n t = \text{constant}$$

where P is pressure and t duration. The most widely discussed version of this relation is the critical energy fluence concept (Walker and Wasley, 1969) where $n = 2$, but numerous other values have also been utilized by other workers.

1. Small Scale Tests.

A very large number of tests have been developed to assess SDT sensitivity of energetic materials. The largest collection of such tests are variants of the gap test, the most widely used (and misused) of which is the NOL large-scale gap test (somewhat of a misnomer since the charge diameter is approximately 1 1/2 inches and it is the prototypical small-scale test; see Price et al., 1974, among many). After many years of use, this test still presents an extremely difficult challenge to modelers, with different attempts producing significantly different results. The major difficulties are relevance of test size (ratio of charge diameter to critical diameter), difficulty in modeling, and undue reliance on negative results (the 70 card criterion defines hazard classifications for 1.1 (mass detonating) versus 1.3 (mass burning) propellants). Although many elegant tests have been developed

to measure SDT including ones employing multiple Lagrange gages (Cowperthwaite, 1973), most tests are marginally instrumented and suffer from the limitations thus imposed.

Other tests that are commonly accepted and have some advantages (mostly being easier to model than gap tests) are the wedge test (Majowicz and Jacobs, 1958; Gibbs and Popolato, 1980), the minimum priming test (Gibbs and Popolato, 1980) or some variation of a flying plate test. While these and other tests are adequate, the data are subject to misinterpretation and abuse and thus are not definitive in themselves. Many compilations of results of these and other tests exist (Gibbs and Popolato, 1980; Dobratz, 1974; and others). None of these compilations should be used indiscriminately, suffering from data of varied quality, sketchy test descriptions, and similar names used for differing tests. In short, all of the difficulties that beset datum bases are present.

2. Large Scale Tests

Very little SDT testing is done on a large scale. What is done falls into two broad categories, gap tests done on the order of several inches diameter and munitions testing which utilizes actual or generic hardware to test systems vulnerability. In the first case, the system is not fundamentally different from that in the NOL LSGT or the Expanded Large Scale Gap Test (Liddiard and Price, 1987). In the latter case, the test configurations and hardware are not standardized, which makes comparison of results difficult at best.

3. Selected Results

SDT thresholds are a function of many variables, some relative to the test methodology such as the amplitude and time of the pressure pulse and properties of the materials themselves. The effect of test parameters can be seen in Figure 4 which shows the relation between the 50% gap thicknesses for four explosives as measured in the NOL LSGT (charge diameter 1 1/2") and NOL ELSGT (charge diameter 3"). Figure 4 is taken from Liddiard and Price (1987). A similar pressure-time variation for a different, flying plate test is shown in Figure 5 which shows an explicit pressure-time plot for initiation of a cast-cured explosive containing 84% RDX (data from Belanger et al., 1985).

Effects of material properties, such as particle size, can be seen in Figure 6, which shows the effect of particle size on the run distance to detonation in explosive wedges initiated by 8 mm flying plates. The data are from Moulard et al. (1985).

C. Deflagration to Detonation Transition (DDT)

As the name implies, the concern is with how detonation of energetic material results from an initial burning reaction. The key requirement for this transition to occur is a large surface to volume ratio and porosity of the energetic sample (Figure 7) either through manufacture and loading in the case of some gun propellants, through large scale damage in the case of missile propellants, or through porosity in pressed explosive charges.

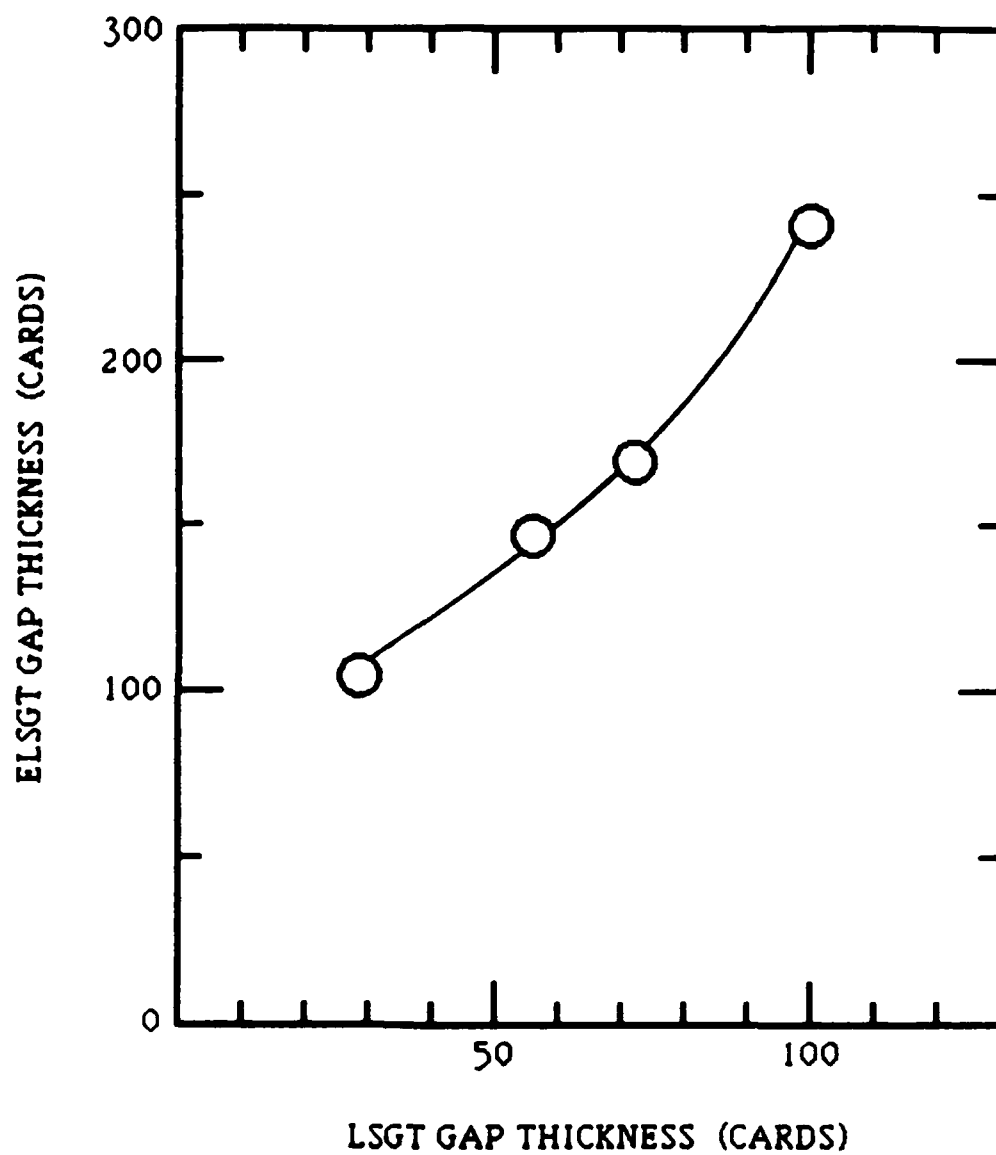


Figure 4. Expanded large scale (ELSGT) versus the large scale 50% gap thickness (LSGT) (from Liddiard and Price, 1987).

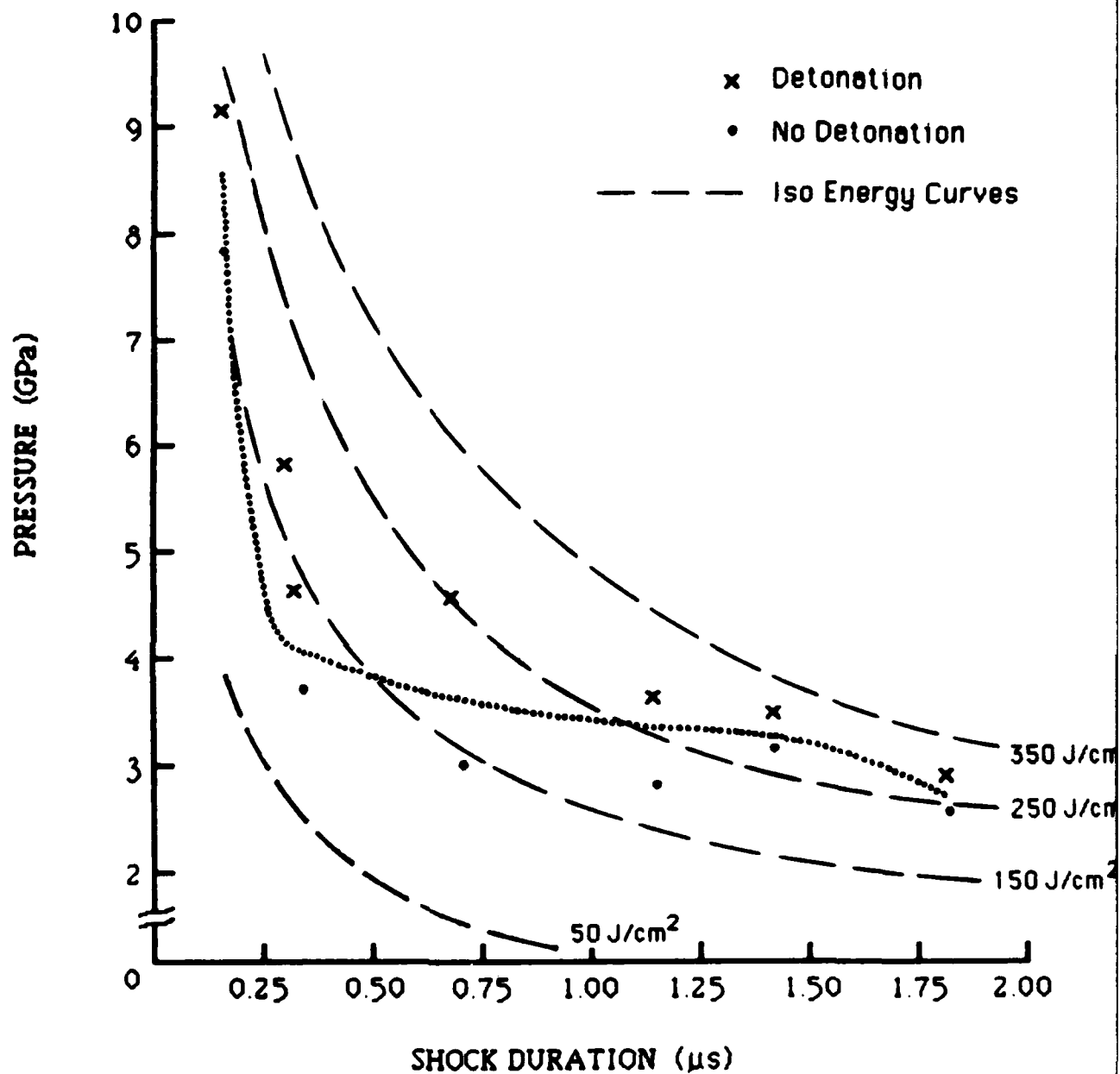


Figure 5. Shock sensitivity of CX-84A to the flyer plate (from Belanger et al., 1985)

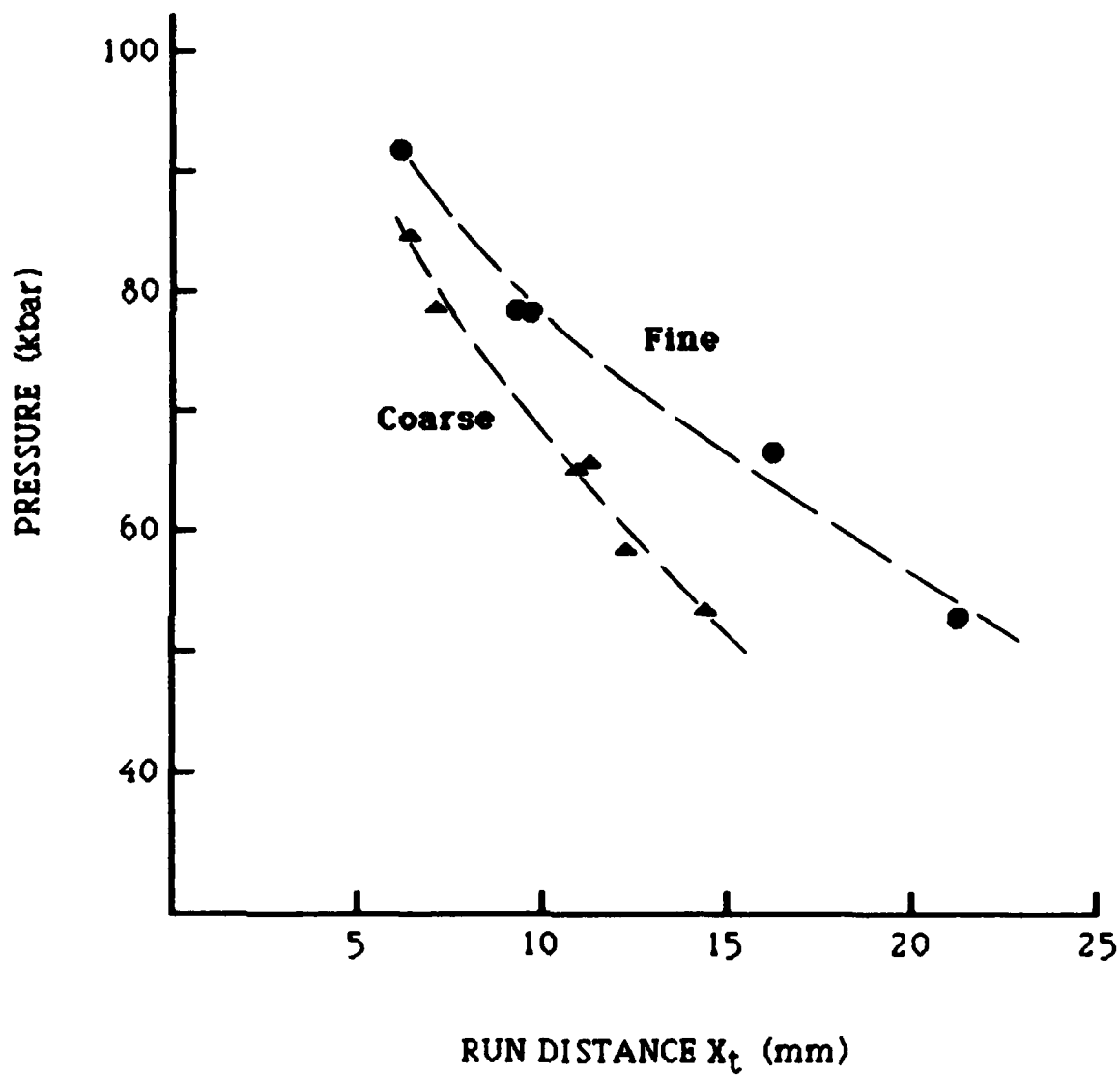


Figure 6. Run distance to detonation versus sustained shock pressure (from Moulard et al., 1985)

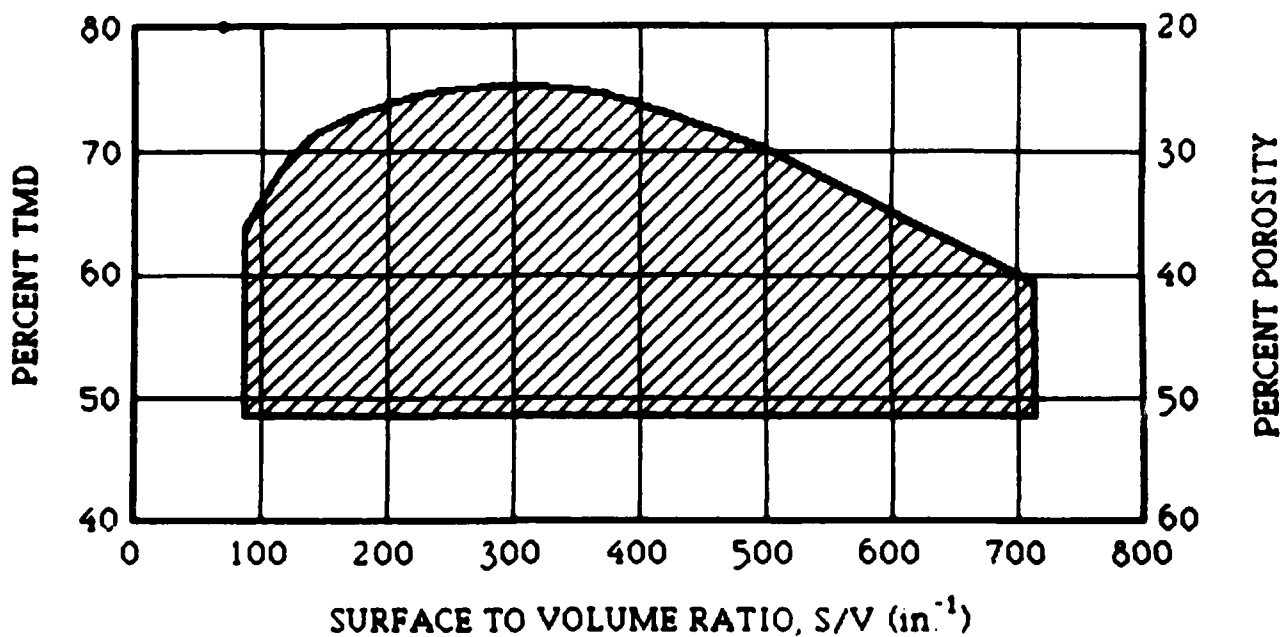


Figure 7. Limits of DDT for a granulated propellant sample, for one propellant in one apparatus. Other propellants in other apparatus may have different values. Plots of this type may oversimplify the issues of mechanical properties and/or crystal imperfections (from Butcher et al. as cited by Bernecker, 1984)

In the past deflagration-to-detonation transition was thought to be: (1) "normal" or "laminar" or "cigarette" (all equivalent) burning of a bed of propellant followed by (2) a transition to "convective combustion" where the combustion penetrates into the bed. This accelerated burning was thought to (3) cause the formation of shock waves which strengthened and (4) led to detonation. Recent work has shown this description to be too simplistic. There is not one single path but a multitude of paths that can result in detonation following some combustion reaction. These multiple paths include:

1. The situation described above. This situation occurs with "soft" igniters (Butcher et al., 1982; Butcher, 1982; Butcher and Isom, 1982) and materials that pyrolyze readily but whose reaction of the pyrolysis products to final products (hence energy release) is "slow" so that energy storage may occur (Boggs et al., 1982, 1984; Price and Boggs, 1985).
2. A variant of the above description with the "convective combustion" (actually several, simultaneously occurring processes) causing compaction of material ahead of the combustion region. This situation is characteristic of tests with "hard" igniters (Bernecker et al., 1976, 1982; Bernecker and Price, 1975; Price and Bernecker, 1975; Bernecker 1978, 1984).
3. Plug driven reactions, with the plug formed either by a separated combustion reaction (Campbell, 1980; McAfee and Campbell, 1986) or by a piston projectile (Sandusky and Bernecker, 1985; Sandusky, 1983).

1. Tests

Various tests are used to determine the susceptibility of energetic materials to DDT. The tests determine the ease with which the energetic material may be damaged (referred to as the "toughness" of the material in the propellant community) and once damaged how easy it is to transition from burning to detonation in the various paths.

The toughness is usually determined using the shot gun test. In this test a sample of propellant is fired at various velocities from a gun (shot gun) at a rigid target. The resultant damaged sample is then collected and fired in a closed bomb and the pressure-time history measured. Data are presented in several ways:

1. Relative Quickness - For a given run the maximum relative quickness, dp/dt , is determined. A high value of relative quickness shows a large amount of damage, or poor "toughness."

2. Critical Impact Velocity (CIV) - The rate of maximum pressure rise as determined from the closed bomb testing is plotted versus the velocity of the sample before impact. From that plot, the velocity corresponding to a dp/dt of 2.5×10^6 psi/second is chosen to be the "critical impact velocity" (CIV). The 2.5×10^6 psi/second number comes from some studies that showed that a dp/dt of 2.5×10^6 psi/second was required to product DDT (Gould, 1980).

3. Burn Area - A data reduction technique, CBREDII (Price et al., 1979) has been developed that gives the burn area as a function of time and distance burned, as well as characteristic dimension of the damaged material. This technique requires two sets of combustion bomb experiments to yield burn data, one with undamaged and one with damaged samples.

Tests to determine the ease of transition from burning to detonation are usually done in a tube configuration with different stimuli. Various igniters have been used - ranging from "soft" to "hard" (see references cited above) to start the material in the end of the tube reacting. Driver sections, a burning material separated from the rest of the bed by a gas impermeable barrier, have also been used as the stimulus (Campbell, 1980). Green et al. (1981) and Sandusky used a piston moving into the tube to study compaction driven DDT (Sandusky and Bernecker, 1985; Sandusky, 1983). Instrumentation in these various experiments included strain gauges and pressure transducers, high speed cinephotography, flash x-ray and event pins (ionization and/or closure pins). Data obtained include pressure-time-distance, event-time (e.g., ionization front as a function of time), and compaction (density) profiles.

Other experimentation is done in support of DDT modeling. These efforts include compaction studies (Sandusky et al., 1982; Elban et al., 1981; Elban, 1986), ignition and transient combustion (DeLuca et al., 1976; Gerri et al., 1974; Krier et al., 1976), permeability and drag (Atwood et al., 1986; Kuo and Nydegger, 1978; Jones and Krier, 1983; Ergun, 1952), burn rates (Boggs et al., 1977, 1980; Parr et al., 1982), flame spread and burning surface area.

2. Selected Results

The pressure-time history of a DDT reaction shows several regions: the ignition, slow combustion build-up, combustion coupled with weak compaction wave, combustion coupled with strong compaction wave, shock formation, and detonation. The location of these events in the p - t plane is strongly influenced by several considerations. These include the degree of confinement, the strength of the ignition stimulus, the sample thermochemical and physical characteristics, the charge dimensions (diameter and column length), and the intrinsic detonability of the material. The physical characteristics of the sample include the size and shape of the damaged pieces, the porosity and gas permeability, and the compressibility. The thermochemical considerations include the chemical composition of propellant, pyrolysis products, and final products, the kinetics and energetics associated with the pyrolysis (solid propellant going to reactive intermediate species) process, and the kinetics and energetics associated with the conversion of the reactive intermediate gases to final products.

It must be stressed that the above items are listed separately but in fact the DDT process is a highly coupled interaction of these various considerations.

D. Delayed Detonation (XDT)

The term XDT has been used to describe the results of some shock and impact initiation experiments on energetic materials in which detonation was

observed to occur at initiation stimuli levels less than the normal values for SDT and at times longer than usual for SDT detonations. Typically, in impact tests, XDT can occur at up to 50% lower impact velocity and exhibit detonation at 25 microsec after impact versus 4 microsec for SDT. The X in XDT reflects the uncertainty in the knowledge of the exact mechanism of initiation. It appears that there is a similarity to both SDT and DDT in some aspects of XDT and that there may be differing initiation mechanisms depending upon the material, its state (solid versus granular), and the input stimulus or experiment.

1. Tests

XDT has been observed in NOL card gap (Keefe, 1981), "shotgun" (Blommer, 1982) and impact (Green et al., 1981) tests with solid and granular explosives. Typical results are discussed below.

2. Selected Results

Figure 8 shows the results from the NOL large-scale card gap test for an explosive which exhibits XDT. From 130 to 160 cards the material displayed a monotonic decrease in the occurrence of detonation as the attenuator card thickness was increased. The resultant detonations occurred within 19 microsec after ignition. This behavior is that normally observed for SDT events. However, as the attenuator thickness was increased beyond 160 cards, a rise in the detonation probability was observed and detonations occurred more than 45 microsec after ignition. This marked departure from normal SDT behavior is representative of the XDT phenomena observed in card gap tests.

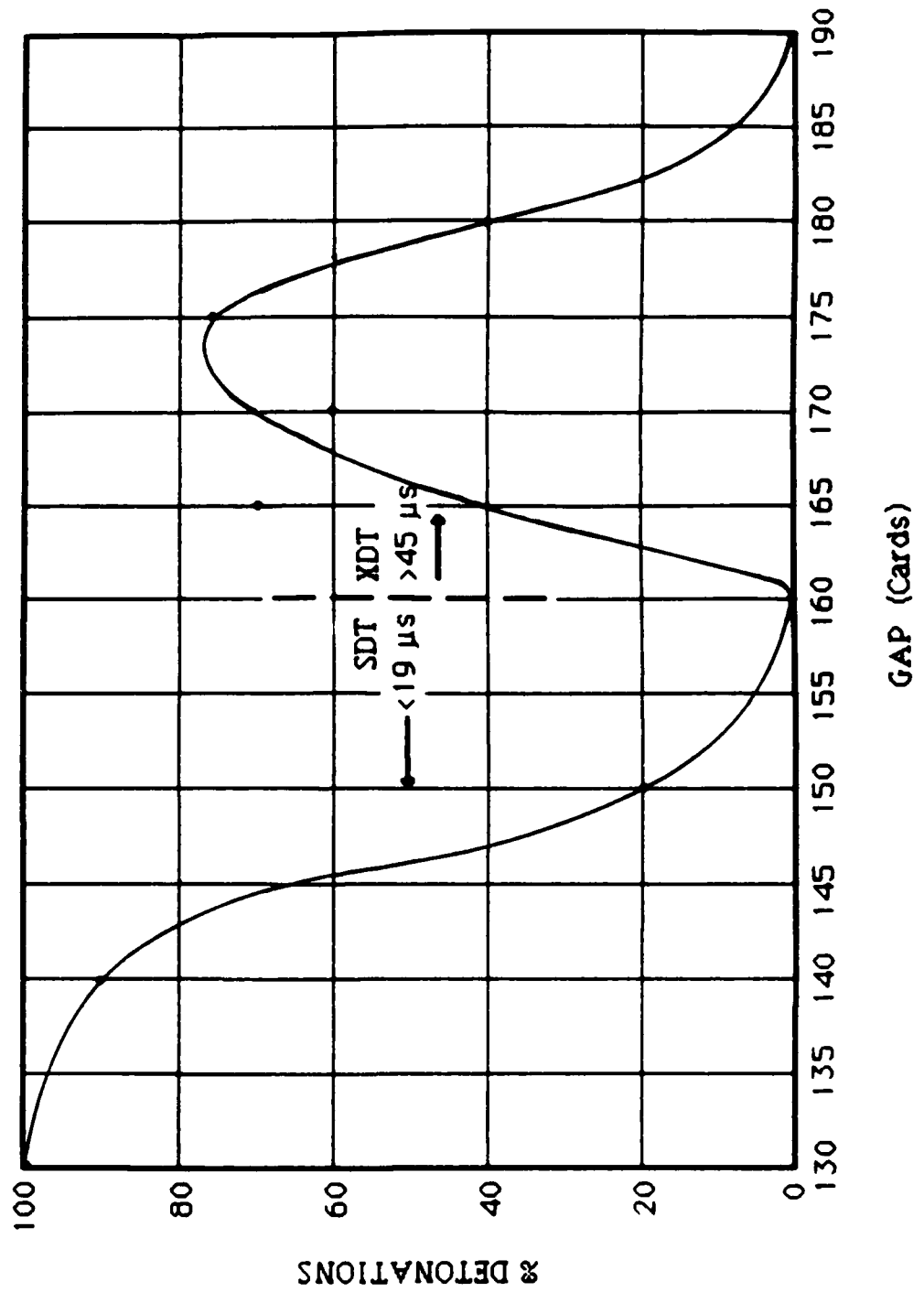


Figure 8. Card gap test results showing SDT and XDT
(from Keefe, 1981)

An extensive series of shotgun tests has been conducted at Hercules to study XDT. The conventional, 12 gauge shotgun, firing 8 gm of explosive, was found to be inadequate to study XDT, presumably due to the small sample size. A majority of the tests was run using a 25 mm gun, with some tests done using 70 and 155 mm guns. Figure 9 shows the impact velocity and resultant over-pressure observed in the series of tests. The observed reactions have been classified as SDT, XDT or deflagrations based on the time interval from impact to detonation and the extent of damage to the target. Figure 10 shows the dependence of the impact velocity threshold for XDT (i.e. the lowest velocity for which XDT was observed) as a function of sample diameter. Clearly there is a marked size dependence below 70 mm diameter.

Impact of projectiles into solid and granular propellants has also been used to study XDT. Results on solid materials have shown both a size and velocity dependence for XDT with larger samples requiring lower impact velocities. In comparison with the shotgun test results, the impact induced XDT evidenced detonation at substantially longer times, typically hundreds of microsec.

It should be noted that the results discussed above are the outcome of tests conducted to investigate the XDT phenomenon. XDT is not routinely incorporated into most propellant hazard test sequences.

E. Thermal Response and Ignition

The response of an energetic material to a given thermal stimulus (accidental or deliberate) is clearly one of the most important

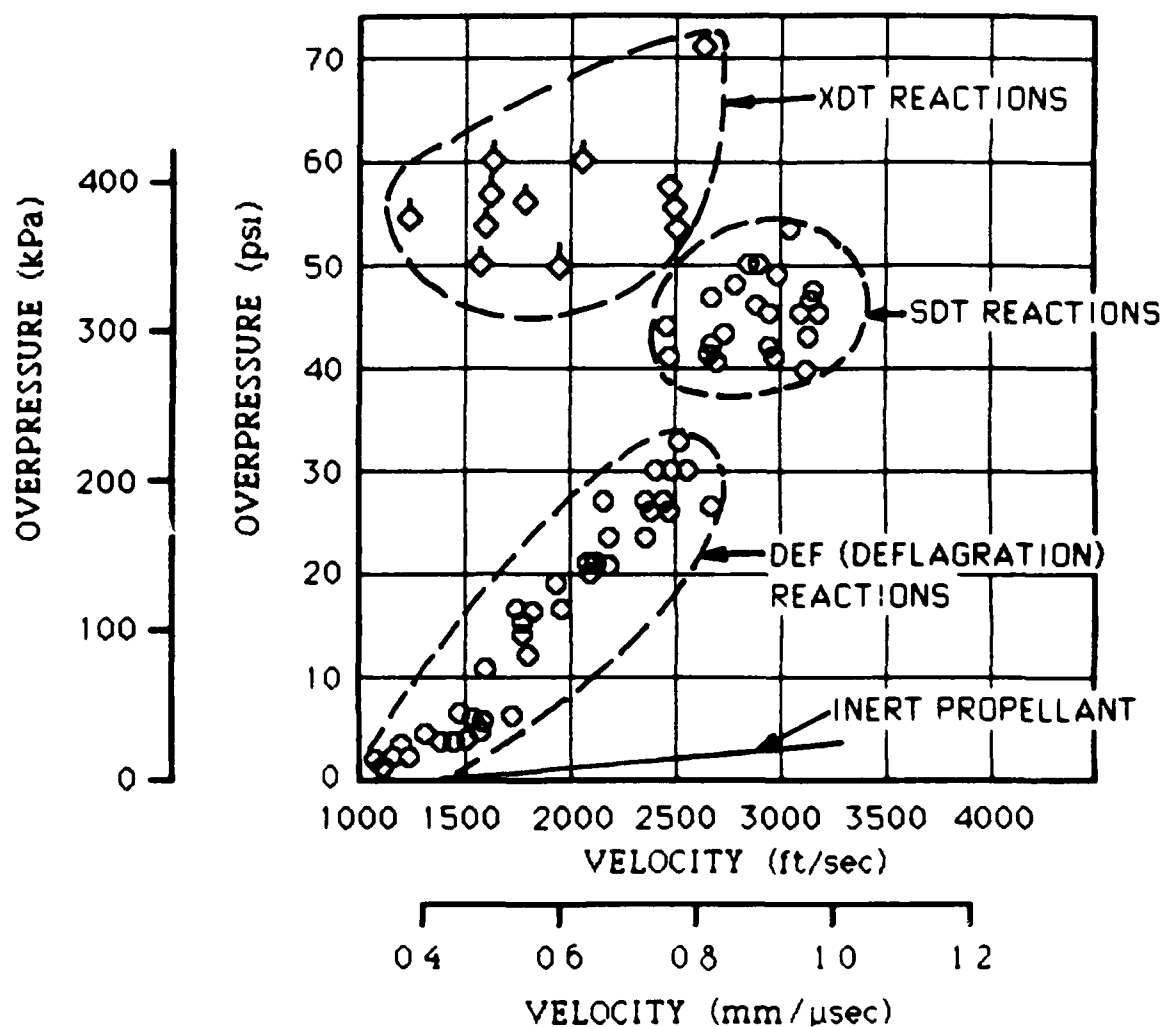


Figure 9. Overpressure versus velocity for direct impact tests. Lines on XDT datum points imply higher overpressure than indicated (from Blommer, 1982)

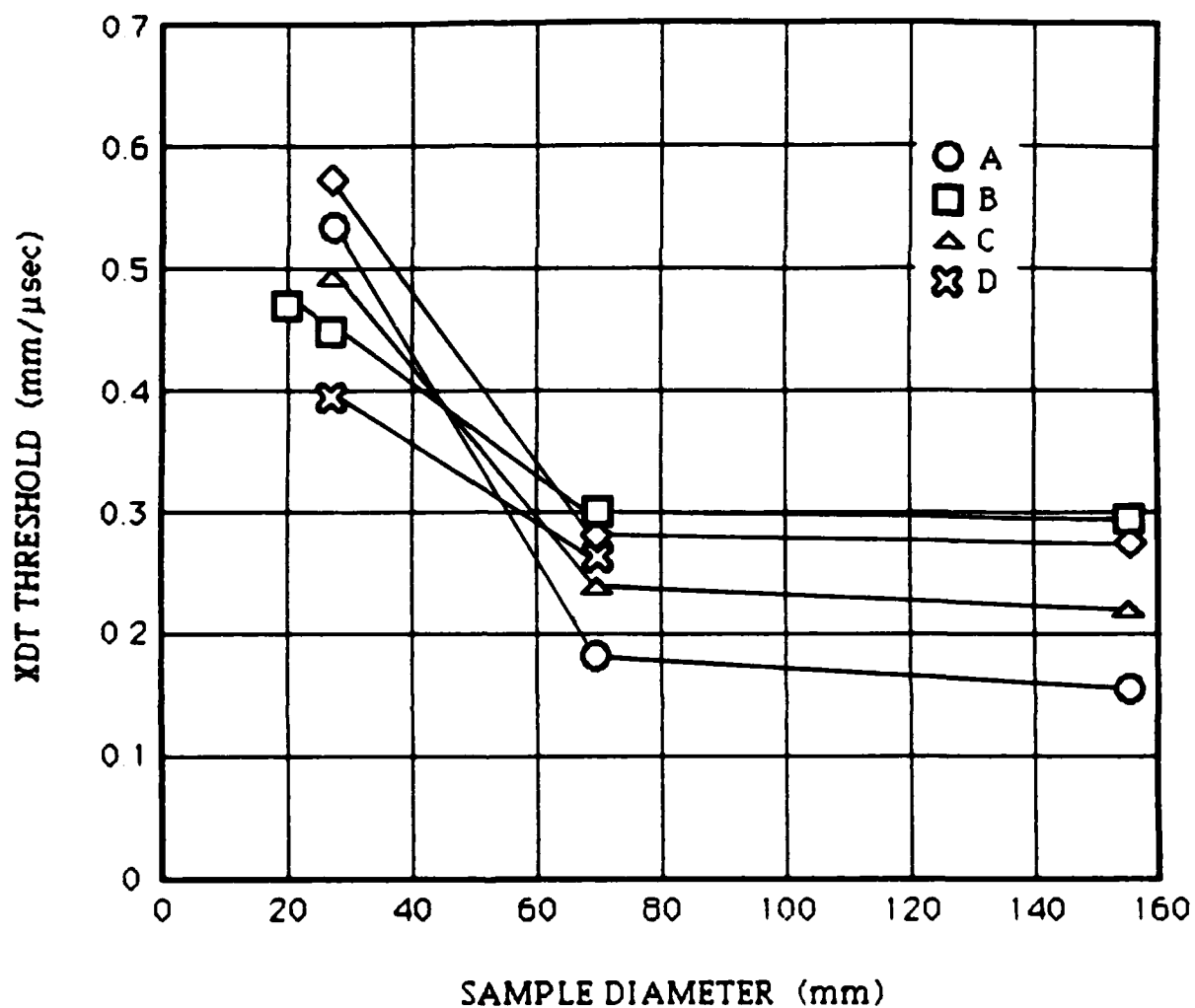


Figure 10. Dependence of the velocity threshold for observation of XDT on sample diameter (from Blommer, 1982)

determinations to be made in the process of evaluating and utilizing that substance as a propellant or explosive. The scale of the sample and the evaluation test varies from milligrams in the case of initial laboratory synthesis to thousands of kilograms for a full-scale production article cookoff test.

The thermal stability and ignition sensitivity of newly synthesized chemicals must be determined before larger quantities are made. Initial thermal stability testing identifies rate of decomposition, phase changes, weight loss, gassing, time-to-explosion, etc.

The thermal response of explosives and propellants is the central factor in all hazardous initiation scenarios. Work done on the energetic material through processes such as friction, shock loading, and electrostatic discharge is converted into thermal energy absorbed by the propellant through conduction, radiation, or convection. Understanding basic thermal initiation mechanisms is necessary to fully account for the behavior of energetic materials to the other stimuli discussed in this chapter.

1. Small Scale Tests (Rogers and Janney, 1983)

If the heat produced by the decomposition of an energetic material cannot be dissipated as rapidly as it is formed, the charge will self-heat to ignition, explosion, or detonation. Critical temperature, the lowest constant surface temperature at which a given material of specific size and shape will

self-heat catastrophically, is a useful concept for determining the safety of a particular formulation.

This concept can be modeled mathematically. Experimentally derived values, related to the kinetics constant of the energetic materials, can be input to the models and used to predict critical temperature. Extraction of these kinetics parameters from small-scale test data is very difficult, however.

The complexity of most decomposition processes makes it dangerous to predict the safety of large-scale operations on the basis of untested, unconfirmed models. The predictive models must be tested against completely independent small and large-scale self-heating tests to confirm prediction accuracy.

There are many small-scale thermal stability tests used in the propellant/explosives community. A brief description of the more commonly used methods follows:

1. Differential Thermal Analysis (DTA): determines the difference in temperature between a sample and a thermally inert reference as a function of temperature as the system is heated at a linear rate. The DTA can be used to determine the onset of an exotherm, which depends on programming rate, intrinsic stability, and chemical mechanisms. DTA determinations of complex decomposition reaction kinetics are highly suspect. Unless confirmed by independent thermal tests DTA results must not be used to predict the thermal behavior of materials.

2. Pyrolysis, or Effluent Gas Detection: detects decomposition products in the gas stream as a function of sample temperature. This method also cannot detect many decomposition mechanism changes, and cannot be used to determine reaction kinetics. It is a useful method for determining impurities and solvents and allows heterogeneous reactions to be detected.

3. Thermogravimetry (TGA): measures sample mass loss at a linear heating rate. This method is not suited for mechanistic studies, but because it is set up for rapid testing, it can serve as a screening tool for widely different formulations. Accurate measurements of sample mass are a problem; very rapid decomposition processes may cause mechanical loads on the mass measurement device, producing erroneous mass values over time.

4. Vacuum Stability Tests: heat the sample at a constant temperature and draw off volatile or product gas for determination of volume and/or composition. Modifications to the vacuum stability tests include Chemical Reactivity Tests (CRT) and Taliani Tests, which maintain pressure in the sample's vicinity.

5. Henkin Time-to-Explosion Tests: attempt to measure limiting conditions for catastrophic self-heating small-scale for laboratory use. These tests measure time-to-explosion of propellants and explosives at a constant sample size and shape. They provide a useful relative scale of thermal hazards. Confined samples are dropped into a preheated metal bath and the time-to-explosion is measured at progressively lower temperatures until the lowest temperature giving an explosion is found. For energetic materials the

time-to-explosion test provides the simplest measure of critical temperature, allows formulators to choose optimum candidates, and usually turns out to be the most important single test run on a new energetic material.

6. Differential Scanning Calorimetry (DSC): holds a sample and reference at exactly the same temperature and measures the energy necessary to maintain the temperatures the same. There is no heat flow between the sample and reference, so quantitative measurements can be made at constant sensitivity.

DSC measurements are well-suited for reaction rate determinations. Incompatible additives can be detected by observing changes in rate processes. Measurement of the kinetics properties of an incompatible system enable quantitative predictions of thermal hazards. The accuracy of the predictions based on DSC measurements can be tested against experimental critical temperature measurements.

7. Accelerating Rate Calorimetry (ARC): attempts to maintain a sample in an adiabatic state and permit it to undergo thermal decomposition due to self-heating while recording the time-temperature-pressure relationship of the runaway process. ARC measurements made at constant, high pressures allow pressure effects on elementary and secondary reactions to be measured, thus complementing DSC determination of kinetics constants.

These more-or-less standard laboratory stability tests are supplemented by many more specialized thermal tests. These tests vary from facility to facility and are used when specific material applications are intended. Thermal tests for quality control, aging and stability, and mechanical response are quite numerous, and are usually unique to a single facility.

Small scale ignitability tests, particularly for propellants, have become quite sophisticated. Radiant energy, in the form of heat and light, is applied to propellant samples in a controlled manner. The heat flux can be controlled both in terms of intensity and sample area heated. High power lasers and arc-image furnaces are used to provide a fairly constant and measurable heat flux. Propellant ignitability is determined as a function of applied energy, external pressure, and time. Test devices are now sophisticated enough so that fundamental kinetic rate processes can be determined from properly instrumented experiments. Such devices are also used to study the transition to stable combustion and the changing chemical reactions which accompany that transition (Boggs et al., 1984).

2. Large Scale Tests (Hannum, 1985)

Large scale tests for thermal response usually are component specific. There does not exist a standard thermal test for weapons systems because thermal environments are diverse. The thermal environment of most concern for weapon designers is cookoff. The entire weapon system is subjected to a severe thermal environment representative of an actual accident. This environment usually pertains to a fuel fire in the vicinity of an operational weapons system. An example of such a test for a pool fire environment is one in which a component is subjected to a 30-minute sustained black-body heat flux from a JP-4 fire (1850 F).

The primary cookoff process is energy transport from the heat source to the weapon system at a level sufficient to initiate the various and simultaneous transport processes that eventually cause mechanical failure. Although there are well established computational codes that can predict temperature histories in complex geometries for a variety of thermal boundary conditions, no predictive capability exists to determine the nature of the cookoff event (deflagration versus detonation) in its entirety. Including the thermomechanical response of the explosive and the structural response of the confinement to predict the time-to-ignition requires a considerable degree of known information regarding geometry, material properties, thermal boundary conditions and the rate dependent chemistry.

At present, empirical predictive methods based on well characterized systems are fairly well understood. Modeling has been investigated, but has not proved to be especially useful. Highly innovative small-scale cookoff methods have been developed and empirical analyses exist, but they still lack first-principle analyses leading to prediction techniques.

3. Selected Results

Small scale laboratory methods are suited for drawing preliminary conclusions about the relative sensitivity of various materials. The literature is filled with studies of this type. Reports on time to explosion (Zinn and Rogers, 1962) and ignitability data (Bradley, 1974) are numerous and widely available. Such data are very useful when selecting candidate formulations for different applications.

Results for large scale tests (cookoff) are much more system specific. Large scale tests are often performed as part of weapon qualification programs and the results can seldom be applied to other systems. An excellent review of present cookoff analysis and test methods is available (Hannum, 1985).

4. Parametric Studies

The problem of thermal initiation, particularly for solid rocket propellants, lends itself well to parametric studies. Lab-scale thermal stability and time-to-explosion tests require small propellant samples and short experimental run times. Large datum bases are generated during most propellant development efforts for the effects of ingredient changes on thermal stability and aging. A systematic parametric approach can also help identify decomposition mechanisms, identify interactive catalytic effects, and quickly pinpoint ingredient incompatibilities.

Parametric studies are particularly useful for ignition. Devices based on arc-image furnaces or lasers, which supply a controlled source of thermal energy to a test sample, are well suited for evaluating the effects of a large number of variables. Ignitability test programs typically vary ambient pressure, sample temperature, thermal intensity and wavelength, and sample formulation (ingredients, particle size, etc.).

Parametric studies are much more difficult when large quantities of energetic materials are involved. Some systematic testing on small scale cookoff devices has been done, but these efforts have been limited to specific

propellants or explosives intended for a particular weapon system. Most cookoff tests are done for full-scale rocket motors or bombs. These items are already extremely expensive and to perform any kind of meaningful parametric studies of propellant properties or confinement effects is beyond the budgetary scope of most weapons systems programs. At this level, modeling efforts based on a fundamental understanding of decomposition mechanisms and thermomechanical response are much more meaningful and cost effective.

F. Friction

In the handling of energetic materials, friction is probably the most difficult to eliminate and the least understood of all the hazardous stimuli encountered. Friction is usually present in some form through handling, pouring, mixing or packaging, or is associated with sliding, rotating, pressing or scraping movements of handling devices.

In simplest terms, friction is the resistance to relative motion between two bodies in contact. The amount of friction depends upon the materials which are in contact and the condition of the sliding surfaces. Friction between surfaces is due to the condition of adhesion and plastic deformation. Adhesion, the tangential force required to break the attractive force between surfaces under a normal load, is usually the more important factor. Plastic deformation is caused by the ploughing, grooving, or cracking of surface asperities.

Although major advances in the understanding of frictional phenomena have occurred during the past few decades, energetic materials have not normally been the subject of investigation. Testing and safe handling techniques are highly empirical. It is difficult to devise a test which delivers a simple frictional stimulus without indirectly heating it by contact with other sliding components of the apparatus. At present, there is no standard friction sensitivity test as almost all test apparatus in current use were designed and fabricated by government laboratories or private industry to perform tests for their internal purposes. However, the basic principle of any apparatus is that a test material is subjected to frictional forces generated between two surfaces. Although in principle the tests are similar, the parameters vary. The motion between the two surfaces may be linear or rotary, single-pass or continuous. The test sample may be in solid or powdered form or mixed with an abrasive. The criterion for a positive reaction can be (as sensitive as) the detection of forty parts per million of combustion products via gas sampling or (as insensitive as) the presence of flash, spark, burn, or odor.

There are many varieties of friction sensitivity tests. These tests can be grouped into three categories:

1. Those which shear a thin layer of energetic material between two rigid plates of steel or other material of construction; some machines impart linear, or single-pass motions, and some impart rotary or continuous motion;
2. Those which rub a block of material violently on a hard or abrasive surface;

3. Those which subject a sample to extreme deformation in an impact or extension event.

Most friction sensitivity test apparatus are small scale tests which fall into the first category.

1. Small Scale Tests

a. Pendulum Friction Tester

The pendulum friction apparatus is based on the design originated by the Bureau of Mines in 1911, which measures the response of energetic materials to the combined effect of friction and impact stimuli. The original Bureau of Mines apparatus consists essentially of a fixed steel anvil and a weighted pendulum (20 kg) with an interchangeable face of steel or hard fiber, called a shoe. The pendulum rod is two meters long. A 7 gram powdered sample is spread evenly in and about the grooved position of the anvil. The pendulum is released from a fixed height and subjects the sample to a series of glancing, rubbing motions of the shoe as it sweeps back and forth across the powder about 18 times before coming to rest. A test sequence consists of ten consecutive trials with the steel and fiber shoes. The reaction that could occur is characterized as either unaffected, crackles, burning, or explosion. A material passes the friction test if there is no more than a crackling sound in ten trials with the fiber-faced shoe regardless of the behavior under the action of the steel shoe.

A variant of the pendulum friction device has been developed at the Naval Weapons Center. It consists of a steel striker plate and a steel striker wheel attached to the end of a weighted pendulum (1.8 kg). The energetic material powder is positioned on the striker plate in such a manner that the striker wheel, when released, makes initial contact with the powder two degrees before bottom dead center and passes through the entire sample. The pendulum drop height corresponding to the 50% probability of initiation and/or the pass-fail criterion are used to measure the friction sensitivity. The criterion for a positive reaction is any evidence of a reaction as judged by the test operator with his senses of sight, sound, and smell.

b. Sliding Block Friction Tester

Sliding block friction testers represented by the Alleghany Ballistics Laboratory (ABL) and Julius Peter (BAM) designs are being used by both government and industrial laboratories.

In the ABL tester, a sample is subjected to frictional forces generated between two hardened steel surfaces. The lower surface is a movable anvil, a sliding block on rollers. The upper surface is a stationary wheel. A known force is applied hydraulically to the sample through the stationary wheel. A weighted pendulum is released from various predetermined angles so that it strikes the end of the movable block, imparting various known velocities to it, in the range from four to ten ft/sec. The wheel and anvil materials can be varied to simulate in process frictional forces being assessed. The criterion for a positive reaction varies from one organization to another.

The criterion can be as quantitative as the detection of forty parts per million of gaseous combustion products or as qualitative as the presence of a flash, spark, burn, or odor. The result is recorded in terms of the maximum force which can be applied to the wheel without causing the sample to react in twenty trials after at least one positive reaction occurred at a test level one increment higher. The 50% value is also reported by some companies.

In the BAM tester, a powdered sample (about 25 mg) is subjected to frictional forces generated between two roughened porcelain surfaces. The lower porcelain plate is attached to a platform which is moved once to and fro at a constant velocity of 4.7 to 5.0 cm/sec over a 10 mm path by means of an electric motor. The upper surface is a small, stationary, cylindrical, porcelain peg. A known load is applied to the sample through the stationary peg. A positive reaction of the test sample is determined by the presence of odor, flash, spark, and/or noise. The results are recorded as the 50% probability level of initiation and/or the 10% probability of initiation. The 10% probability of initiation is defined as the force that is one level above the load at which no ignitions occurred in ten trials.

c. Rotary Friction Tester

The Rathsburg rotary friction tester consists of two steel discs with polished surfaces. The lower disc is stationary, while the upper rotates at 80 rpm. Test material is mixed with finely pulverized sand and placed between the discs. Known loads are applied. If an ignition is observed, the test is repeated using successively smaller loads until a weight

is reached with which no ignition takes place. The energetic material is considered insensitive to friction if no ignition occurs after twenty revolutions in six trials at the maximum load. A variant of this tester using higher rpm and different sample configurations has been developed at Aerojet Strategic Propulsion Company.

In the Naval Ammunition Depot friction design, a hardened, stainless steel friction rod spins on top of a powdered sample in an aluminum holder. The friction rod is held in the chuck of a drill press which serves as the driving force for the rod. The rotational speed and loading of the friction rod can be varied. Frictional energy transmitted is calculated from measurements of the reaction torque on the sample holder. The time to a positive reaction is measured. A positive reaction is noted as a flash, smoke, or an audible bang.

In the Esso friction tester, sometimes called a screw friction tester, a small disc of energetic material is held between two stainless steel platens. The upper platen is screwed down against the lower fixed platen by manually driving the lead screw with a torque wrench. The torque is increased until an ignition occurs. The criterion for an ignition is a flash or sound. If no ignition occurs, the test is repeated with glass grit added to the sample. If no ignition occurs with the glass grit, the test is repeated with diamond or silicon carbide grit. The number of trials conducted and the types of grit used depend upon the company conducting the tests.

2. Large Scale Tests

While some large scale tests have been done in the past there are none in common use at present. Generally the large quantities of material involved and the difficulty of controlling, instrumenting and analyzing large scale friction tests preclude their use as research and development tools.

3. Selected Results

An extensive statistical analysis of friction (and other hazards sensitivity test) results is being conducted by Schwarz (1987) at Morton Thiokol for the Army Missile Command, using a strip friction test described in Napadensky et al. (1978). In this method the propellant sample consists of a microtoned 0.02" thick disk placed between two 24 gauge stainless steel strips with grit-blasted surfaces. One steel strip is fixed by means of a clamp, and the other strip is attached to the rim of a rotating wheel. A hydraulic ram is used to apply a normal load to keep the sample and friction strips in direct contact. A weight dropped from a fixed height onto a lever attached to the rotating wheel provides the necessary force to overcome friction and to pull the moveable strip across the sample disk. Ten negative runs, i.e., no scorching, burning, etc., at a fixed normal force are taken to indicate insensitivity to that level of friction.

The hazards testing and analysis is an effort to find ways to reduce the sensitivity of formulations containing the highly effective burn rate catalyst catocene. Ninety four mixes with formulation variations from a baseline

TP-H8295 propellant with both cured and uncured samples are used in the study as shown in the table below:

AP Particle Size and Quantity

200 μm 0 - 34.5% of the formulation

16 μm 0 - 34.0%

1.7 μm 0 - 27.6%

0.9 μm 0 - 34.5%

0.7 μm 0 - 24.4%

Al (30 μm) quantity - 18, 19, 19.5, 20%

Al_2O_3 quantity - 0, 0.25, 0.50, 0.75, 1.0%

Fe_2O_3 quantity - 0, 1, 2, 3, 4, 5, 6%

Catocene quantity - 0, 1, 2, 3, 4, 5, 6%

AP quantity - 66, 67, 67.8, 68, 68.9, 70, 74.8, 75.56, 77%

The interpretation of two different operators is included in the analysis to reveal elements of subjectivity in the testing. A single variable regression analysis with resulting correlation coefficients determined at a 95% confidence level show a frictional sensitivity dependence upon (1) whether or not the propellant is cured, (2) the quantity of 0.9 μm ammonium perchlorate, (3) the quantity of Al, iron oxide, catalyst, and (4) the operator performing the test.

In the testing of uncured propellant with operator #1 the frictional sensitivity was shown to be dependent upon the quantity of catalyst and the 200 μm AP. With cured propellant the same operator measured a frictional

dependence on Al and Fe_2O_3 . Operator #2 measured no frictional dependence with either cured or uncured propellant. The statistical analysis is continuing with efforts to exclude insignificant quantities that may mask strong correlations.

4. Parametric Studies

In view of the results cited above, it would be premature to select work performed in the past as definitive to the trends in friction sensitivity with various independent variables.

G. Impact

The word impact is used in several different ways in the energetic materials community. Some of the experimental situations to which this term has been applied are the following:

1. Drop Weight Impact. These tests involve dropping large weights (typically 5 kg) on small explosive samples (20 mg-50 mg) which rest on (more or less) rigid anvils. The impact velocity is 1 m/sec to 10 m/sec.
2. Projectile (Bullet or Fragment) Impact. In these tests projectiles are fired at charges which are large relative to the size of the projectile. Impact velocities are in the range of 500 m/sec to 2000 m/sec (or even more in some cases).

3. Low Velocity Impact. In these tests a large projectile (several kilograms) is fired at a large explosive charge. Impact velocities may be in the range of 100 m/sec to 500 m/sec. The work of Napadensky (1965) is a prime example.

4. Susan Impact Tests. This is a well defined test which has been useful in comparing the sensitivity/vulnerability of various explosives. It will be described briefly below.

5. Shaped Charge Jet Impact. Shaped charge jets have small diameters (a few millimeters) but very high velocity (4 to 10 km/sec).

The initiation phenomena which occur in these tests and the mechanisms which operate can be vastly different. In this brief review we will confine ourselves primarily to items 1 and 2, because tests of these types are very common. We will not discuss low velocity impact (item 3 above) and will only briefly discuss shaped charge jet impact as part of a section on projectile impact. The Susan Test will be briefly described because of its utility in comparing several aspects of the sensitivity of materials. Drop weight impact involves only small amounts of material, and the phenomena which are observed do not depend on the final application of the material (gun propellant, rocket propellant, or explosive). On the other hand, the gross loading density and the amount of internal surface area can have major effects on the results of projectile impact tests and shaped charge jet tests, and therefore gun propellants can behave very differently from solid explosives and rocket propellants.

1. Small Scale Tests

Perhaps the most widely used impact test in the energetic materials industry is the drop weight test. Because it is relatively simple and utilizes small inexpensive samples the drop weight test has generated large archives of data.

The test is used: (1) as a screening tool in the synthesis of new materials, (2) for ranking impact sensitivity of energetic materials, and (3) for obtaining explosives hazards classification data according to requirements of the Departments of Defense and Transportation (Anon., 1985b).

A major flaw in the drop weight test is that results do not correlate well across organizational boundaries. The results do seem to correlate satisfactorily within each user organization, so that ranking of materials is possible. This aspect of the test results coupled with its required use for hazard classification testing serves as the momentum for its continuation. In reviewing the questionnaire responses and noting the reported variations in procedure and devices one wonders that any correlation at all is possible. Although attempts at standardization have been made (ASTM, 1984), there appears to be little uniformity of procedure or machine design.

Within the testing community are found many variations of the drop weight tester; however all operate on the principle of a weight falling through a guide system and impacting a sample of material placed on an anvil. An intermediate striking weight may or may not be used to impact the sample. The use of sandpaper on the top (striking surface) of the anvil has been

reported to reduce the variation in obtaining the 50% probability of reaction height, H_{50} . The grain of sandpaper to be used has not been standardized.

The DoD Explosives Hazard Classification Procedure, TB-700-2, specifies that impact tests are to be conducted using a Bureau of Explosives Apparatus of which two different sizes are required. The smaller device is used for the more sensitive energetic materials. If the sample is a composite propellant, the larger 25 lb, 6 ft apparatus is recommended. The ASTM designation E680-79 does not require rigid standardization of the apparatus, but discusses in considerable detail the proper limits on many design considerations. A description of the Bureau of Mines Impact Apparatus is included. Both tests are in use as well as others built by Technoproducts, Olin Matheson, or by the user installation. It is probably safe to infer that all devices have been modified or custom designed to meet user requirements and may therefore bear little resemblance to one another.

Reaction detection is a major source of inconsistency and concern to users. A positive reaction produces one or more of the following phenomena: (a) flash or visible light, (b) audible report, (c) smoke (not dust), or (d) decomposition revealed by discoloration of the sample with the sound of a positive reaction. Because of the subjective nature of deciding whether a reaction is positive or negative, tests results become highly operator dependent. Most respondents cited operator dependency as a major source of deficiency in the impact testing. Some efforts are reported in which phototransistors, IR sensors and/or pressure sensors are used to detect positive reactions and thereby eliminate operator dependency (Coffey and DeVost, 1986).

The mechanism of initiation under drop weight impact has been studied by several investigators, with the work of three groups particularly well known. Field and his coworkers at Cambridge (Heavens and Field, 1974; Field et al., 1982, 1985; Swallowe and Field, 1981), Coffey and his coworkers at the Naval Surface Weapons Center at White Oak (Coffey et al., 1979; Coffey and Armstrong, 1980; Coffey and DeVost, 1986; Coffey et al., 1986; Coffey, 1985), and Afanasev in the Soviet Union (Afanasev and Bobolev, 1971) have made important contributions. We will summarize only a few salient points from this work here.

All three groups recognize the importance of plastic work in heating the explosive to its initiation point, and all recognize that the sample must fail and flow in order for this to occur. Afanasev notes the importance of the melting point and the effect of impact pressure on the melting point. In a study that was not directly related to impact tests, Frey (1981) noted that viscous processes could produce temperature well in excess of the melt point in a shear band. Pressure was also very important in this case because the viscosity of organic liquids depends strongly on pressure.

The Field group and the Coffey group observe that the sample fails (as shown by stress records) and flows (as shown by photography) before initiation occurs. Coffey has usually observed that reaction first occurs towards the outer edge of the expanding disk of test material. The strain rate at this point is higher than in the center, but the pressure is presumably lower. Field has observed the same trend in many experiments, but has also seen reaction begin closer to the center in some cases.

Coffey et al. (1986) have recently done some tests where they used drop weight heights above the height for 50% initiation. By monitoring the velocity of the falling weight and the thickness of the sample, they were able to determine the energy dissipated by plastic work in the sample at the time of initiation. For several different heights, the dissipated energy was about the same (within a factor of two) for different impact heights and velocities. With freshly polished anvils, the dissipated energy at the time of initiation was a factor of seven (roughly) higher. These results confirm the importance of plastic work, but they also confirm the importance of localization and of the details of the flow process.

Coffey (1985) and Frey (1981) have tried to model what may happen in a localized zone of high shear. Coffey's model considers the effect of solid state dislocations. It notes that as the solid deforms, the dislocations tend to pile up at crystal boundaries. When a critical stress level is reached, the locations begin to move, and there is an avalanche of moving dislocations which causes rapid local heating. Frey's analysis is in terms of classical physics (heat conductivity, viscosity, yield strength, plastic work). Both models predict rapid heating in highly localized bands, but direct comparison with drop weight impact tests is not possible.

2. Large Scale Tests

In this section we consider the impact of relatively high velocity projectiles (bullets, fragments, or shaped charge jets) on explosive samples which are larger in thickness and diameter than are the projectiles. There

has been a tremendous amount of work done in this area, and no attempt will be made to survey it all here.

Some of the best early work was done by Dewey and Slade (1957) and Brown and Whitbread (1961). They did numerous experiments where they fired right circular cylinders at bare and lightly covered explosives (the cover plate thicknesses were generally less than the radius of the projectile). The projectiles impacted on the flat end of the cylinders. They observed that the critical velocity for initiation of the sample was independent of the length of the projectile (as long as the length was greater than about one half of the diameter). When the material of the projectile was changed, they observed that the velocity required for initiation changed in such a way that the impact shock pressure remained constant. Thus, it appeared that the initiation was caused by the impact shock wave, and all of the considerations of shock initiation should apply. In the context of these experiments, initiation should be interpreted as initiation of detonation. The charges were basically unconfined, and when detonation did not occur, the explosive was shattered and thrown about the test site. A determination of how much material may have reacted, if any, was not made.

When fully confined charges are impacted, the situation in some aspects is quite different. Howe et al. (1981) have observed that shock initiation alone cannot always explain the detonation thresholds which are observed. They determined the critical velocity for the initiation of detonation in a TNT filled artillery shell and observed, in contrast to the earlier work just discussed, that the initiation threshold depended upon the length of the

projectile. Apparently, in this case some shear effect contributed to the initiation process. Fully confined charges are also subject to a variety of violent, non-detonative explosions. Frey et al. (1980) and Howe et al. (1981) have studied these effects.

Initiation by shaped charge jets has been considered by many investigators, including Held (1983) and Chick et al. (1985). Chick notes that the mechanism of initiation in this situation is a shock. When the case is thin, it is the impact shock which is transmitted through the case to the explosive which causes initiation. When the case is thick, it is the bow wave shock which forms in the explosive in front of the penetrating jet which causes initiation. In considering bare explosives, Held observed that the quantity v^2d , where v is the jet velocity and d is the jet diameter, is about constant at the critical point for initiation. Since the mechanism is shock initiation, the relative sensitivity of explosives to jet initiation should vary as their shock sensitivity.

The Susan Test is described by Green and Weston (1970). In this test, a 0.45 kg explosive charge, confined in a light aluminum case, is put on the front of a massive steel projectile, and the resulting projectile is fired at a steel wall. Blast gauges are placed at prescribed distances from the impact point. The measured blast overpressure is used as a rough measure of the violence of the reaction. The results are usually presented graphically and show the impact velocity where reaction begins and the rapidity with which the reaction builds up as the impact velocity increases. At high velocities, shock initiation may come into play. At lower velocities, the charge gets

pinched between the wall and the steel plug at the rear of the projectile and is subject to high rates of deformation. Thus, several aspects of sensitivity are brought into play in one test, and the test has been a useful way of comparing explosives.

3. Selected Results

Results obtained with large-scale impact tests have been discussed in the previous section. For drop weight testing, the objective is to determine the 50% probability height or H_{50} at which reaction occurs. The Bruceton or up and down method is the recommended procedure for determining H_{50} . Other data recorded include the minimum potential energy for initiation and the 3.75 inch and 10 inch results required for explosives hazard classification. While most of the test objectives are basically the same throughout the industry it may be interesting to note how the results are evaluated by two different organizations (see table below). One must wonder if the differences shown may be attributed to machine-to-machine variations or to the manner in which the data are interpreted.

<u>RESULTS</u>	<u>INTERPRETATION A</u>	<u>INTERPRETATION B</u>
>50 kg-cm	Relatively Insensitive	-
15-49 kg-cm	Sensitive	-
45 kg-cm	Sensitive	Normal Sensitivity
20-45 kg-cm	Sensitive	High Sensitivity
20 kg-cm	Sensitive	Very High Sensitivity
<15 kg-cm	Very Sensitive	-

4. Parametric Studies

In view of the above table, relative rankings within a given organization may provide qualitative insight into the influence of the independent variables. Sample size and preparation are significant contributors to variations in measured results. Such additional factors as temperature, humidity, particle distribution, cure times, hygroscopicity, and ageing should be controlled to prevent comparison of "apples and oranges".

H. Electrostatic Discharge (ESD)

Early in 1985, the U.S. Army experienced an incident with the Pershing II in which a Kevlar-cased rocket motor reacted, killing three people. Ignition of this motor has been attributed to electrostatic discharge through the motor following the separation of dissimilar dielectric materials in a cold, dry climate. Prior to this incident existing ESD testing indicated that this propellant was not sensitive to ESD (see Section 1 below). However, experimentation subsequent to the incident showed that the PII propellant was more sensitive to ESD at colder temperatures (Anon., 1985a). As a consequence of the PII fire there is need to better understand the electrostatic discharge phenomenon in solid rocket motors.

The build-up and subsequent discharge of electrostatic charge on energetic materials used in ammunition and propulsion systems can pose a severe hazard while handling these systems. The hazard arises when energetic material becomes charged to a potential where breakdown of the material occurs or when

a change of grounding conditions allows the discharge of an existing charge on the material. Discharge processes generate charge carriers which in turn reduce the impedance of the energetic material and result in a rapid current increase. This can lead to arcing, establishment and growth of discharge paths followed by catastrophic initiation of the energetic material. Such reactions primarily lead to a pressure and temperature increase in a very narrow discharge path which may in turn induce ignition, sustained combustion, or even detonation. Consequently, it is necessary to study phenomena associated with an electrical discharge as a function of time, temperature, pressure, and composition of the energetic material involved. Some general understanding in the area of ESD hazards and electrical properties can be obtained from Kent and Rat (1982), CPIA (1986), Cantey (1984), Blythe (1979), Griffiths (1981), Montgomery (1959), and Moore (1973).

Recent research on the electrostatic discharge sensitivity of solid propellant samples was begun at Societe Nationale des Poudres et Explosifs (SNPE), France, after they had several incidents similar to the Pershing II. These incidents were experienced in the handling of a aluminized, plasticized hydroxy-terminated (HTPB) or carboxyl-terminated polybutadiene (CTPB) propellant grains. Because of this, Kent and Rat (1982) at SNPE developed a three-part methodology to predict propellant sensitivity to electrostatic discharge.

In an effort to quickly provide rocket propellant manufacturers and end users with a measure of confidence in the ESD sensitivity of their propellants, the French methodology has been applied to U.S. solid rocket motor propellants. The French method includes:

1. A calculation of a percolation breakdown coefficient, P , from the use of Percolation Theory and a factorial investigation of the propellant's active constituents (Hammersley and Handscomb, 1964). Based on experimental results there exists a threshold value for P below which propellants are not sensitive to ESD and above which they are.
2. Measurements of volume resistivity of the propellant specimens as a function of temperature, which also give an indication of the propellant sensitivity to electrostatic discharge. The volume resistivity of all materials fits into one of three categories when its logarithm is plotted versus $1/T$ (T = absolute temperature). As shown in Figure 11, the material can have a straight line behavior; the initial slope can be positive, passing through a transition temperature, followed by a smaller positive slope (M_1 greater than M_2), or the inverse (III). The French determined the propellants which may be ESD sensitive all had a ratio of initial slope to final slope greater than or equal to one. This test can be performed as a function of temperature and relative humidity to locate an ESD threshold.

In order to better evaluate ESD sensitivity, more fundamental propellant properties should be evaluated. Some of the measurements which have been adopted in the U.S. to complement the French work are:

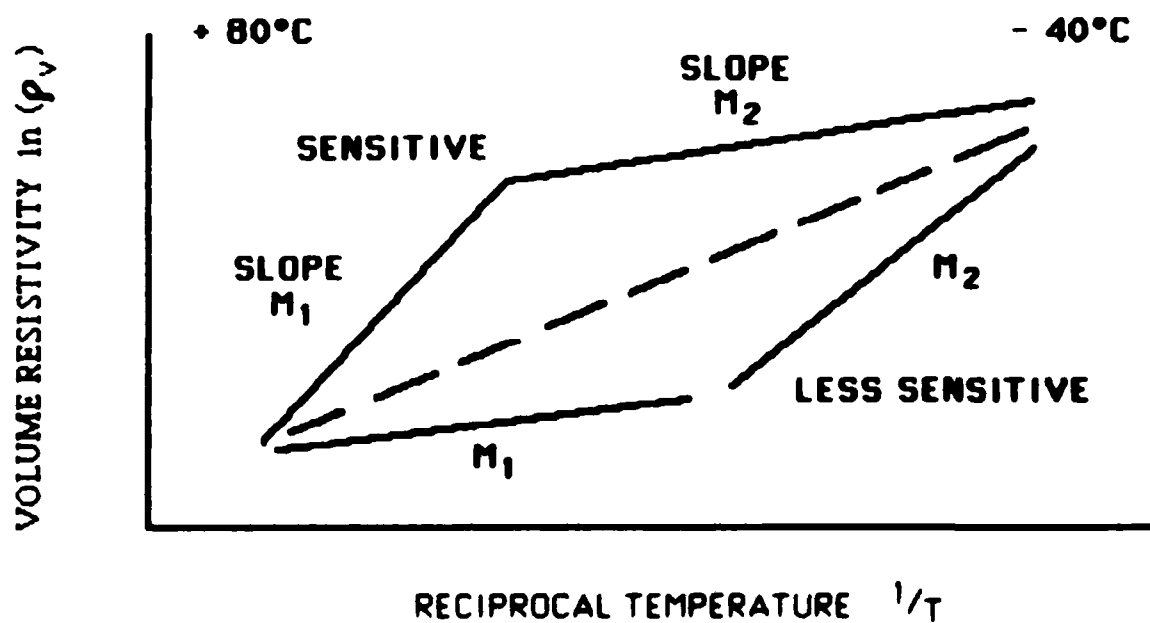


Figure 11. Schematic variation of volume resistivity versus inverse temperature for energetic materials (from Kent and Rat, 1982)

1. Dielectric constant measurement of propellants. The dielectric constant of a material is defined as the ratio of capacitance C when it is present to that when there is a vacuum between plates (C/C_{vac}). Dielectric constant is also known as permittivity or specific inductive capacity.

2. Dielectric breakdown strength. This is defined as the minimum energy needed for a material to break down (make the material conducting).

3. Surface and volume resistivity as a function of time and temperature.

1. Small Scale Tests

Both Government and industrial laboratories have adopted a small scale electrostatic discharge test for energetic materials which is based on a test method designed by the Bureau of Mines (Brown et al., 1953). This test consists of charging a capacitor with a 5000 V direct current power supply, followed by a discharge through the test sample from a known distance. A positive reaction can be a combination of smoke, burning, sparking, or noise, resulting in total consumption of the sample (Lanterns, 1986).

Some of the disadvantages of the 5000 V ESD test (designed for use with primary explosives, not composite solid propellants) are:

1. Test results are laboratory specific since type and extent of reaction are poorly defined, energy and duration can differ, and electrode shape, etc., are not optimized;

2. It is a single discharge apparatus, which is not capable of simulating repeated discharge or constant electric field conditions;
3. The reported energy at which the sample reacts is the energy stored in the capacitor banks not the energy actually absorbed by the sample.
4. The test is conducted under "ambient" conditions. The temperature and humidity are not controlled. Tests are not made at low temperature.

In addition it is clear that electrical property measurements are required for propellants, including surface and volume resistivity as functions of time, temperature, applied voltage, and relative humidity (ASTM D257, plus research methods). There are several methods of measuring dielectric constants for materials (ASTM D150). In the case of propellants the frequency dependence, temperature, and humidity effects have not yet been determined.

Finally, another parameter required is dielectric breakdown strength (DeButts et al., 1986; Hermesen et al., 1986). For propellants the following parameters should be studied and reported:

- Optimum electrode design,
- Sample size,
- Temperature,
- Voltage Ramping Conditions,
- Breakdown Path,
- Current flow profiles, and potential correlation with thermal ignition thresholds.

2. Large Scale Tests

Kent and Rat (1982) have recommended a large scale RC discharge test for evaluating the ESD hazard sensitivity of propellants. This test has become known as the "French Test" and consists of discharging 30 kV with a theoretical energy of 15.6 J through a propellant cylinder 9.0 cm in diameter by 10.0 cm tall. A typical test consists of 30 consecutive 15.6 J (30 kV and 34.4 nF) discharges on each of three identical specimens. If any of the 90 discharges results in cracking, popping, smoke or fire, then the propellant is considered sensitive to ESD.

Disadvantages which have become apparent are: a) a large sample is required; b) the test is empirical; c) the baseline is considered to be ambient temperature; d) only Go/No Go results are obtained; e) and the understanding as well as datum base for this test is limited.

3. Selected Results

Preliminary results have been reported primarily in CPIA (1986), obtained since the PII incident. Earlier work is reported in Cantey (1964). Since existing small scale test methodology did not suggest any special difficulty with spark sensitivity for the PII propellant (DeButts et al., 1986), and current research has not yet identified appropriate replacements (or optimal electrical property determination techniques), no results are presented at this time.

4. Parametric Studies

A variety of parametric studies is being performed within the ESD community. Among some of these are: a) investigation of electrical properties as a function of propellant composition (i.e. solids loading, particle size, etc.); b) time, frequency, electrode configuration, temperature and humidity dependence of resistivity, dielectric breakdown and dielectric constant; and c) applied voltage, sample confinement, sample size, humidity and temperature effects on the "French-like" test. Some early results are available in CPIA (1986).

CHAPTER III. DEFICIENCIES IN PHYSICAL/CHEMICAL MECHANISTIC UNDERSTANDING

The previous chapter served to introduce current hazard test methodology, and results as appropriate for energetic materials. Respondents to the questionnaire were also asked to identify gaps in understanding, the subject of the present section. We follow the same technical organization.

A. Critical Diameter

The critical diameter of an energetic material is a threshold dimension for the propagation of a steady state detonation. As such, it is a fundamental quantity in an engineering sense, but not when viewed from a mechanistic standpoint. As an engineering quantity, it represents the interplay of a variety of fundamental processes: homogeneous and heterogeneous reactions, micromechanical dynamics, etc. From a basic perspective, the critical diameter is a quantity which is related to the more general, shock-to-detonation behavior of the material. A first principles model which could calculate the shock-to-detonation process for an arbitrary geometry would be able to calculate the critical diameter as a limiting case. As is discussed in more detail in the following section, SDT models are not yet to that state of development and require extensive, experimentally-derived input data.

B. Shock to Detonation Transition

On the one hand, the understanding of SDT is quite good. Several tests can be accurately modeled. These include the wedge test, the minimum priming test, and the Lagrange gauge studies among others. Models that have been the subject of serious study include Forest Fire (Mader and Forest, 1976; Forest, 1978) and ignition and growth (Lee and Tarver, 1980) as well as that of Nunziato (Kipp et al., 1981) and Kim (1986), among others. However, there is a much less rosy picture also with respect to models, tests, physics, chemistry and phenomenology.

The essential difficulty is that very little is known of the fundamental processes that are important in SDT whether they be physical or chemical. This is especially true at the microscopic or molecular level. We know of, and can to some extent model, the role of heterogeneity in the SDT process, for example, but it is not clear what the mechanism is. The same situation applies to particle size and shape, the role of defects, temperature, pressure, etc. Nor are the chemical processes of importance known or understood. The "hot spot" model is widely known, yet poorly understood.

Most of the models developed for SDT are empirical and many use radically different approaches. No single model as yet can predict behavior under all relevant conditions. A reviewer of an early draft of this section responded as follows: "... modeling can be viewed good only as applied to engineering calculations and much analysis heavily follows experimental

guidance as opposed to being used as a predictive capability. To address the physical issues, . . . much better combustion models will have to be constructed."

Experimental observations themselves tend to compound our confusion. In Section IIB experimental studies of Belanger et al. (1985) and Moulard et al. (1985) are mentioned. From the first, the following is quoted, "The results obtained up to now suggests (sic) that the shock sensitivity of curable plastic-bonded explosives is reduced when the size of RDX particles is increased . . ." and from the second, "The formulation containing the fine RDX was significantly less sensitive than the coarse RDX." To be sure there are differences in the experiments, pulse widths are somewhat different, 87% RDX versus 70%, etc., but the results are indicative of the care that must be exercised in comparing observations.

A further point is the relevance of SDT testing to hazards evaluation. The validity of extrapolation from a 1 1/2 inch gap test to a 12 inch or 12 foot rocket motor must be based on an understanding of what is tested as well as what is tested for. Earlier mention was made of ramped pulses versus sharply rising ones and one must also include multiple shocks as well. The physical nature of the material also controls its sensitivity, and test results on a homogeneous, nearly voidless test specimen are hardly representative of what would be observed for a granular (damaged) sample.

C. Deflagration to Detonation Transition

Rapid progress in understanding the various processes occurring during DDT has been made in the last decade; however, much work remains to be done. The understanding of compaction behavior has increased markedly (Kooker and Constantino, 1986 and citations in that reference). The importance of using a fully transient combustion description instead of the previously used ignition criteria and steady burning has been recognized (Boggs et al., 1982, 1984; Price and Boggs, 1985).

The modeling of the DDT process has also greatly improved with the increased mechanistic understanding. There are many models now in existence (Baer and Nunziato, 1983, 1984; Baer et al., 1986; Beckstead et al., 1977; Butler et al., 1982; Butler and Krier, 1986; Hopkins, 1974; Kim, 1982, 1984; Krier and Gokhale, 1978; Krier and Keizerle, 1977; Pilcher, 1978; Pilcher et al., 1976, 1977; Price and Boggs, 1985; Weston and Lee, 1985). Most of these models are "first principles" models based on the conservation of mass, momentum, and energy equations. The models try to describe phenomena consisting of highly coupled interactions between gasification of the solid, flow of gases past solids causing compaction, compaction restricting further flow, and reaction of gases with various (thermal and mechanical) energy release mechanisms. A complete description is impossible (and probably untractable) and so various constitutive relationships are used to describe the heat transfer, drag, compaction, gasification, etc. The parameters used in these relationships come from the ancillary experiments described in Chapter II.

Most past descriptions of the DDT process have been cast in physical rather than chemical terms. Reactions were assumed to be either "off" or "fully on" with full and instantaneous equilibrium thermochemical energy release. This drove much of the experimental and analytical work. Indeed, experimental measurements largely consisted of wave speeds as determined by strain gauges and ionization or shorting pins down the length of the test bed. It has only been recently that pressure transducers have been used. The analyses were primarily the prediction of shock wave speed and amplitude.

Deficiencies in Experimental Work

Damage: The entire DDT process is predicated on having a high surface to volume ratio, and sufficient shock sensitivity of the energetic material. For solid rocket propellants this requires damage, and in some cases rather extensive damage, of the propellant. This is the first and key consideration.

While we use tests such as the shotgun to give a ranking of an energetic material's toughness or resistance to damage, we do not obtain much fundamental understanding from these tests. We must understand the mechanisms causing damage: how is damage formed (e.g., dewetting of crystalline ingredients from the rubbery matrix), what type of damage is formed, and to what extent.

DDT Tube Experiments: Most of the DDT tube studies have been done using idealized systems: ball powders, HMX particles, cut or shredded propellant. These studies provide insight, but we also need to test real propellant

having real damage. Additional work with simple systems is required to provide further fundamental knowledge.

Tests need to be better instrumented especially to detect and follow the thermochemical reactions. It has only been recently that pressure transducers and flash X-ray (to detect and follow compaction) have been used. We need to start measuring temperatures and hopefully someday have an indication of what species are present.

There is also a need to start measurements at time zero, not just near the detonation transition event. It is the processes occurring early in the event that set up the DDT.

Collaborative Experiments to Provide Constitutive Equations and Parameters for These Equations

The various models, while starting with descriptions from first principles, must resort to constitutive relations to describe portions of the overall process. For example, relationships are used to describe the compaction of the energetic material and the concomitant changes in porosity and intergranular stress. The constitutive relations used require data from experiments to evaluate the parameters in the expressions and to determine the applicability of the relationship (is the relationship of a general nature, is it only applicable to one material, or is it only applicable to a certain range of conditions). We greatly need these data in the various areas listed below:

1. Dynamic as well as quasi-static compaction data on a wide range of materials, including both real propellants and simpler to understand model systems. There is a need for compaction data for materials which fracture.
2. The gas flow-compaction interaction. The drag-compaction-permeability experiments presently being performed need to be extended to higher Reynolds number flow.
3. Reaction of the solid. Previous models largely focussed on the hydrodynamics of the process often to the almost total neglect of the chemistry and thermodynamics of the reactions. Reactions were described as either "on" or "off" with (1) full and instantaneous equilibrium energy release at a rate given by a pressure dependent "burn rate" while in the "on" condition and (2) an artificial ignition criterion (e.g., threshold surface temperature) as the switch between off and on. While such schemes are mathematically convenient they mask the reality of the DDT processes.

Specifically the kinetics and energetics of the transient combustion reactions of the various energetic materials need to be determined in the relevant regimes: slow heating rate experiments and steady state burn rate studies are largely inapplicable. (Note however that steady state burn rate data as a function of pressure and initial sample temperature are useful when coupled with a fully transient combustion analysis to evaluate the non-time-dependent terms.) Data which have been used in the past include ignition maps (flux, time to reaction, type of reaction (ablation versus self-sustained ignition), and pressure), and the pressure and temperature dependence of burn

rate. Additional data describing the species produced and temperatures involved in these transient reactions are desired.

Finally, there is a need to decouple the mechanical phenomena (compaction, fluid flow) from the reaction aspects wherever possible and study each separately, and then merge the phenomena in a step-wise fashion.

Deficiencies in Analyses

The constitutive relations discussed above need to be improved in scope and application, with better parameters and definition between regions. The relationships ought to be "proofed" against a wide variety of materials and under several conditions. The more wide-ranging these proofing experiments become, the more credible the claims of applicability and scope become.

The analyses, if they are to describe the entire DDT process from ignition to detonation, must include a better description of the thermochemical energy release. Models which use an ignition criterion (such as critical surface temperature) followed by full and instantaneous equilibrium energy release associated with solid energetic material reacting to gaseous final products at a rate given by a simple pressure dependence ($\dot{r} = aP^n$) are really only describing a portion of the DDT problem. These models must be modified to describe the energy release associated with transient combustion.

The analytical models must have better success in describing various parts of the DDT process. In particular, the models need to be able to

describe the various experiments where one part of the process is suppressed while another portion is investigated. For example, the piston compaction with delayed reaction experiments and the early transition combustion initiated by weak ignitor experiments need to be modeled.

The gas flow behavior is another area of deficiency. The models should be capable of handling gas flow in an empty tube (a limiting case), gas flow in a rigid nonreacting bed, gas flow in a compressible nonreacting bed, and gas flow in live beds in the piston driven compaction tests, convective combustion tests, and DDT tube tests.

D. Delayed Detonation

While initially unknown, the mechanism of initiation in XDT is now somewhat better understood, and at least qualitatively has shown similarities with both SDT and DDT. A summary of the area has been recently presented (Butcher et al., 1983).

XDT has been shown to require both a minimum initiation energy and a minimum sample size. The energy is required to fragment or substantially damage solids and to initiate thermal reactions in solid and granular materials. The substantial time delay exhibited by XDT reflects the time necessary for these reactions to build into a combustion wave, driving the material to a detonation in a manner similar to DDT. A minimum sample size is needed to guarantee containment and prevent quenching taking place before the combustion wave can lead to detonation. As shown in Figure 12, XDT is

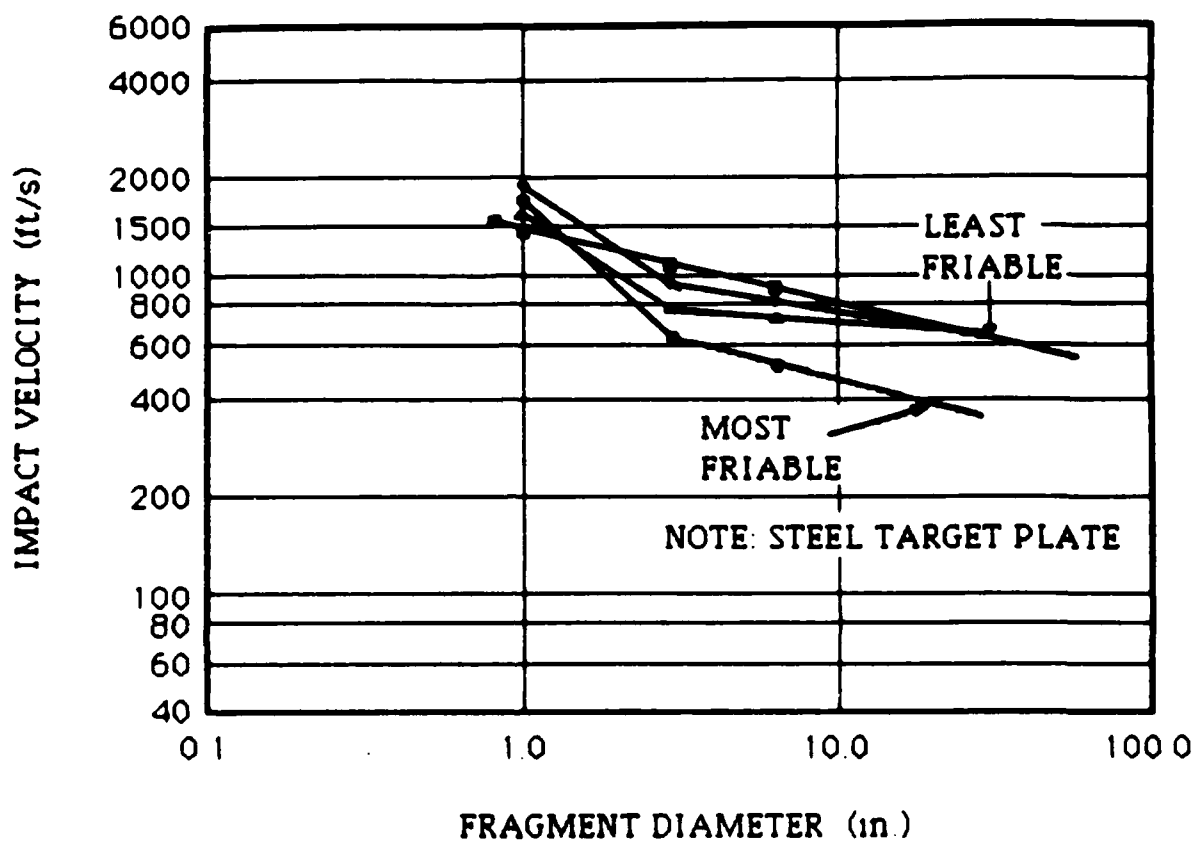


Figure 12. Effect of impact fragment size on sensitivity to XDT (from Butcher et al., 1983)

affected by material friability (ease of breakup under impact) and sample size. Small samples of the most friable materials are more resistant to XDT since they more easily break up and, thus, do not provide the necessary confinement. At larger sample sizes, however, the more friable materials are the better candidates for XDT. Modeling of XDT (e.g., Baer et al., 1982) has been able to demonstrate the competition between the developing combustion wave and the quenching effects of rarefaction but must rely on ad hoc assumptions about the behavior of the material under initial impact and the initiation of combustion.

The prediction of XDT requires realistic models for material behavior at high rates of loading, subsequent fracture, ignition and flame propagation. The initiation of ignition by hot spots may be a phenomenon shared by XDT and other processes. The critical issues appear to be those relating to the dynamics of the impact of the material, the mechanisms of material fracture, and the reactivity of fractured material.

E. Thermal Response and Ignition (Baer, 1986)

A major deficiency in understanding thermal response lies in the lack of knowledge of the chemistry of condensed phases, particularly solids that undergo energetic phase transformations at elevated pressures and temperatures. Secondly, the thermal properties of energetic materials in pressed and granular forms are not well defined and often blends of materials are used that further complicate material descriptions. Finally, thermomechanical and thermokinetic analysis will have to be coupled to

determine the mechanical response following initiation. It is these areas of basic research that will improve our understanding of the thermal response and ignition of energetic materials.

F. Friction

The friction area is beset with difficulties. There exist too many test procedures, none of which is modeled to separate frictional effects from those of heating the specimen by adjacent affected surfaces and from impact. Also, working definitions of ignition are qualitative due to lack of suitable instrumentation. Until these deficiencies are resolved, no preferred method for assessing sensitivity to friction will emerge.

G. Impact

A major deficiency in the understanding of drop weight impact results is the problem of small sample response. The heterogenous nature of most solid energetic materials leads to inherent statistical variation of response even within the same mix. It is generally accepted that initiation in the sample begins at localized "hot spots" whose origins have not been fully determined. Speculation is that hot spots may be caused by adiabatically heated gas in voids or in naturally occurring porosity. Another theory holds that hot spots may be highly sensitive particles, e.g., nitrocompounds, which are plastically deformed at rates high enough to cause ignition. A microscopic view relates explosive decomposition under shock to electronic states excited during the impact event. Until the initiation process is better understood, the difficulties in controlling sample variation in impact testing will likely continue.

Another deficiency in the understanding of impact machines is related to the partition of the H_{50} potential energy between the sample and the energy dissipated in the device during impact. A significant part of the H_{50} energy is not used to initiate the sample although H_{50} is commonly reported to be the energy required for initiation. As noted in Section II, Coffey et al. (1986) show the energy required to deform and ignite the sample is relatively constant over a wide range of impact energies and velocities, but requires proper instrumentation for its measurement.

A complete theoretical study of the drop weight impact process has not been done. The yielding and flow which occur are obviously very complicated, being influenced by surface friction, the stress/strain/strain rate behavior of the material, and the yielding of the drop weight (or striker plate) and anvil. Stress, strain, and strain rate undoubtedly vary with both radius and time.

Nevertheless, useful measurements can be made with impact testers. Kamlet (1960) and later Storm (1986) have shown good correlation of H_{50} impact results with the oxygen balance (calculated at CO equal to zero) within given classes of energetic compounds. The more closely related compounds were found to show better correlation. For example, a group of trinitrobenzenes (TNB, MATB, DATB) indicating a correlation of .99 with H_{50} was used to predict the impact sensitivity of TATB.

With regard to the large scale bullet and fragment impact tests, the shock initiation mechanism is the best understood, but even here there are

uncertainties which have been discussed elsewhere. We mentioned in Chapter II that macroscopic shear (associated with the penetrating projectile) seems to be involved in the initiation of detonation in some cases, but we do not understand the conditions under which this happens.

The initiations which do not involve SDT are less well understood. In some cases localized shearing of the explosive in the vicinity of the case/explosive interface apparently causes ignition. A thorough understanding of this requires a knowledge of the stress/strain/strain rate behavior of the material at elevated pressures. At the moment we do not have a good test which ranks explosives in the order of their shear sensitivity.

After ignitions occur in a confined charge, it is important to know how they burn. Burn rates at elevated pressures are also an area of uncertainty. Some materials deconsolidate as they burn, generating large surface areas and the possibility of a transition to detonation; others do not. We do not know what controls the deconsolidation. Penetration mechanics may also have a bearing on what happens. In some cases, a rubbery propellant may close behind a small penetrating bullet. This can lead to confined burning and a more violent event. Again, this has not been studied.

Finally, we should point out that most energetic materials are much more susceptible to multiple bullet attack than to a single bullet. The first impact presumably causes damage which sensitizes to the subsequent bullets, but it is difficult to describe the damage or to relate its extent to the mechanical properties of the explosive.

H. Electrostatic Discharge

At the present time there is no one mechanism to describe an electrostatic discharge through a propellant. However, there exist models which describe the behavior of propellant constituents in the presence of an external field. From the practical standpoint, these models suffer from a major drawback since they require the microscopic properties of the propellant. These quantities are not readily measurable. Further study must be done relating microscopic properties to more easily obtainable macroscopic properties of propellants before any mechanistic interpretation of ESD in propellants can complement experimental data.

There is a lack of understanding of the effect of an electric field, such as would result from the presence of a static charge on a dielectric motor case, on solid propellant. It has been proposed that the presence of an electric field across a propellant section might result in the formation of gases, acids, porosity, etc. These changes in the propellant over a period of time (ageing effect) might sensitize the propellant, resulting in an ESD event.

I. Summary

The above Sections A through H have enumerated specific deficiencies in understanding for the technical areas investigated by means of the questionnaire. In the present section, underlying needs for research are summarized in a more general format. This section thus provides a transition between

deficiencies specific to the technical areas and the near- and far-term needs identified in the following chapter.

One aim of hazards research for energetic materials is to provide adequate understanding so that formulations of equivalent or improved performance, but decreased sensitivity can be tailored to a particular application, a direct trade-off in design requirements in many situations. But, there may be exceptions. General deficiencies exist in the areas of chemical kinetics, mechanical and electrical properties, and micromechanics, input energy partitioning, and molecular level decomposition studies. Specific improvements in understanding for each technical area were listed above, as for example ignition kinetics and criteria, burning kinetics, compaction, and gas flow through compacted bed models for UDT.

Common findings in most of the eight technical areas reviewed in Sections A through H are that current test methods are inadequate for hazards characterization and do not clearly relate to practical scenarios. Interpretation of sensitivity test data with regard to assessing the susceptibility of an energetic material to accidental initiation is a complicated and controversial subject and is often misleading. This is because susceptibility is affected by chemical and physical properties, geometry, confinement, density, and particle size/shape/distribution of the energetic material. In addition, it is not always known which of the numerous stimuli, and possible combination of stimuli, are responsible for achieving initiation or the mechanism(s) whereby incident energies may be delivered to the energetic material.

There are numerous types of sensitivity tests which measure the energy necessary to achieve a prescribed initiation response to a particular stimulus. It is not known, however, how to relate the energy from a specific stimulus, such as the gap thickness measured in a shock test or the drop height measured by dropping a known steel weight on an energetic material spread on sandpaper, to the minimal energetic stimulus necessary to cause initiation in loading plant and end item applications. It should also be noted that in some cases different results and reversal in the ranking of energetic materials have been obtained with different types of tests, employing similar stimulus. Parametric studies, ideally involving method of initiation, propellant formulation, geometry, age, damage, initial temperature, initial humidity, and confinement are generally lacking or incomplete. As a result, mechanistic understanding of both initiation and response severity, particularly at the fundamental level, is generally poor. Consequently, hazards considerations have traditionally been incorporated into the design process after the fact.

Within this general framework a review of the preceding eight sections suggests that electrostatic discharge is the least mature technology, whereas critical diameter, shock-to-detonation transition, and thermal response and ignition have received the greatest attention in the past.

The distinction between the initiation requirements and subsequent response of the energetic material is introduced above. It is important because detonation involves a separate reaction rate acceleration (which can be quenched, for example, in samples of size less than the critical diameter).

Within the context of this distinction, there are two additional, long-range goals. The first is a better understanding of the initiation mechanism, quantitative requirements, and potential synergism between the various forms of initiation energy. The goal of this better understanding is a simpler, smaller, and cheaper hazard test method characterized quantitatively by the proper engineering terms. For example, if the equivalency of electrostatic or mechanical initiation to thermal initiation were understood, both in terms of quasistatic energy input (e.g., friction or slow cookoff) and high rate dynamic input (impact or sympathetic detonation) then it could be possible to define a single test for initiation in which the rate of energy transfer and level of initiation stimulus as functions of time are characterized. The input energy could be thermal, mechanical, or electrostatic, depending on convenience. Furthermore, the significant literature on thermal initiation could be applied to mechanical and electrostatic initiation.

Some progress has been made in establishing empirical, but quantitative requirements for initiation of detonation by a shock, for example. The most widely used model of SDT is probably that developed by Charles Forest of LANL (then LASL) and referred to as Forest Fire (Mader and Forest, 1976; Forest, 1978). The input to this model comes from the Hugoniot relationships, the equation of state and the run distance to detonation as measured in the wedge test (Majowicz and Jacobs, 1958; Coleburn, 1960) where the commonly measured values are time, t_s , and run distance, x_s , to detonation as a function of input pressure. Ramsay and Popolato (1965) observed that a plot of $\ln x_s$ versus $\ln P_i$ was linear for many explosives and this is the relationship used in Forest Fire. Briefly, the Forest Fire rate is the explosive decomposition

rate necessary behind a planar shock wave to accelerate the shock wave along the time-distance-degree of reaction curve determined by the Pop-plot and Hugoniot, interpreting the Pop-plot as a shock pressure growth curve.

Although Forest Fire is widely used and quite successful, it suffers from some deficiencies. For predictive purposes the most serious is that the wedge tests need to be run before the parameters of the model can be determined although methods do exist for estimating some of the parameters such as the effect of density. Other difficulties lie with the wedge test itself, which can be very difficult to use with some materials such as granular or damaged samples. Certain other assumptions such as the single step process inherent in the method have been questioned by some workers who prefer a two-step, ignition and growth model (Lee and Tarver, 1980).

The second goal for further research on hazards is improved understanding and predictive capability for the severity of the resulting event, separate from initiation because transition to detonation may be involved. Here it is convenient to think in terms of the classical definitions of deflagration, thermal explosion, and detonation. This usage is preferred because the end result of the combustion process for each case can be estimated reasonably accurately using the conservation equations, provided heat losses are ignored and the confinement of the system does not fail. Under these assumptions, the analysis is the worst case scenario and is not end-system specific.

The distinction qualitatively between these three combustion events is that deflagration and detonation result from a point, line, or surface igni-

tion. Practical applications therefore could be bullet impact, electrostatic discharge, or large fragment impact, respectively, whereas corresponding laboratory situations could involve a focussed laser, hot wire, and conventional shock tube. The resulting combustion wave then propagates into the cooler energetic material. In contrast, thermal explosion can be thought of as a homogenous reaction, in a global sense of uniformly heated material, which ovens or electron beams (McGuire and Tarver, 1981; Stolovy et al., 1981) can provide. Slow cookoff is therefore the practical situation most closely corresponding to thermal explosion, if the temperature is able to equilibrate throughout the energetic material sample as the external heating is applied. There are, however, models for thermal explosion with temperature gradients (see for example Rogers, 1982).

Most of the other practical situations would be expected to result in deflagration or detonation since they correspond to the definition of the mechanism of point, line, or surface ignition listed above. Sympathic detonation, fast cookoff, bullet/fragment impact, and electrostatic discharge fall in this category.

It should be noted that the use of these classical definitions is consistent with the older hazards literature (Elwell et al., 1967), but is not preferred today by the Department of Defense (see for example Taylor et al., 1985; Storms et al., 1984; JROC, 1986; also Military Standard 1648A(AS), DoD Ammunition and Explosive Safety Standards). In the latter, because they deal with end-use hardware, practical results of initiation are included with the definitions of partial detonation, explosion, and burning, as examples.

However, from a propellant or explosive point of view the traditional definitions are superior since they are independent of the actual design of a munition (intended end use, nature and strength of confinement, geometry, etc.).

Some results have been reported which attempt to characterize the type and extent of the reaction which results from impact or shock initiation. For example, Elwell et al. (1967) provide plots of critical initiation pressure for SDT versus sample diameter non-dimensionalized by critical diameter (see Figure 13). Here the propellant formulation, incident shock pressure, and incident shock surface area were varied independently, with the lines representing detonation thresholds observed in the experiments. For projectile impact, Andersen and Louie (1979) present similar severity plots of impact velocity versus projectile diameter which show thresholds for initiation or ignition leading to a deflagration at lower velocities and a detonation at higher velocities. A typical result for a particular composite propellant of fixed sample diameter is shown in Figure 14. Finally, both Keefe (1981) and Lee et al. (1984) have noted qualitatively that XDT occurs at lower impact pressure than SDT; other data of this type are discussed in Chapter II D. These are valuable first steps at characterizing the limits of response for energetic materials.

In a similar fashion, it is known that in premixed gases detonation requires more ignition energy, more confinement, and more stoichiometric mixtures than deflagration. In both cases, for premixed systems and energetic materials, it is of interest to formulate more quantitative criteria for initiation to a specific result, both experimentally and numerically.

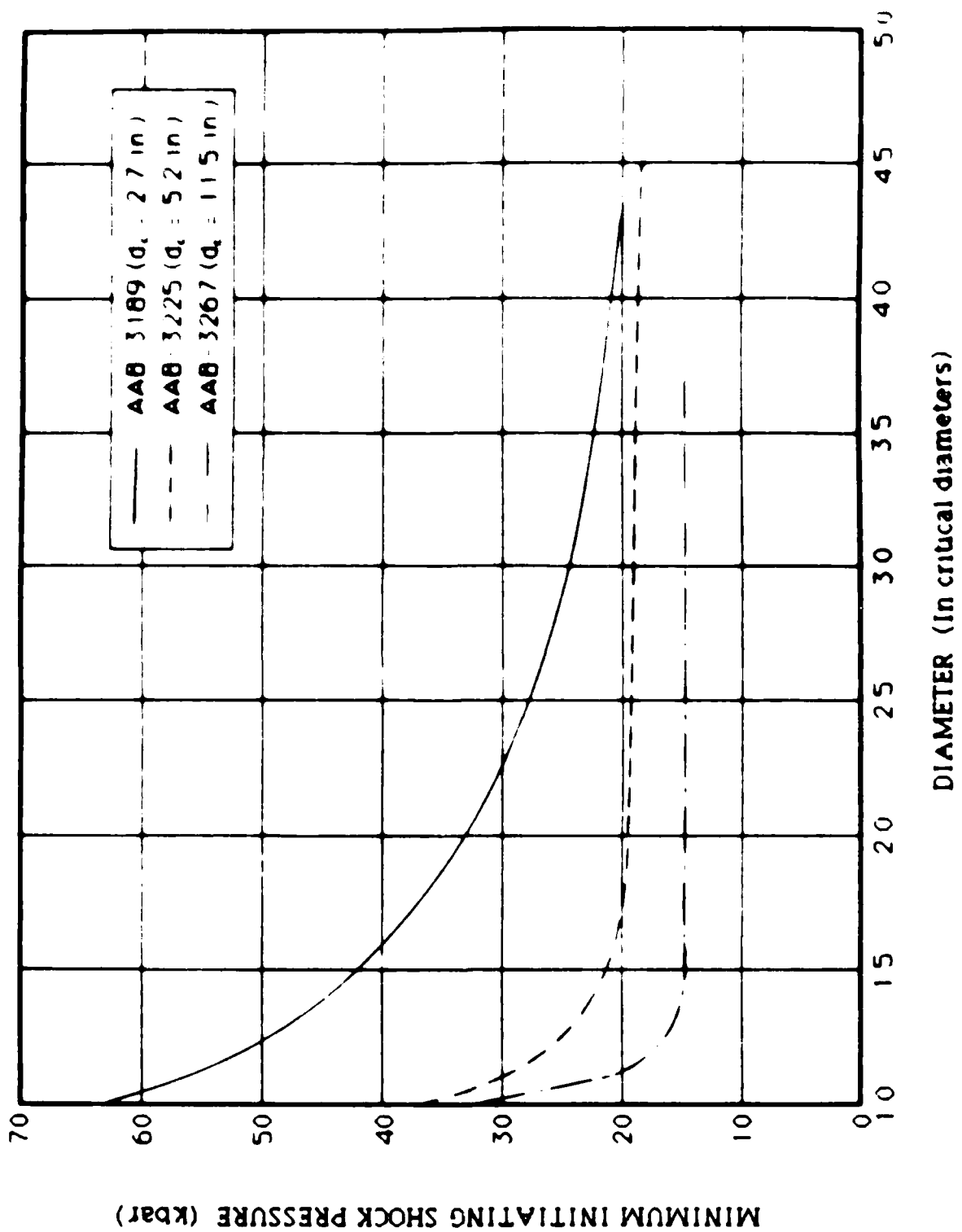


Figure 13. Normalized initiation criteria (from Elwell et al., 1967)

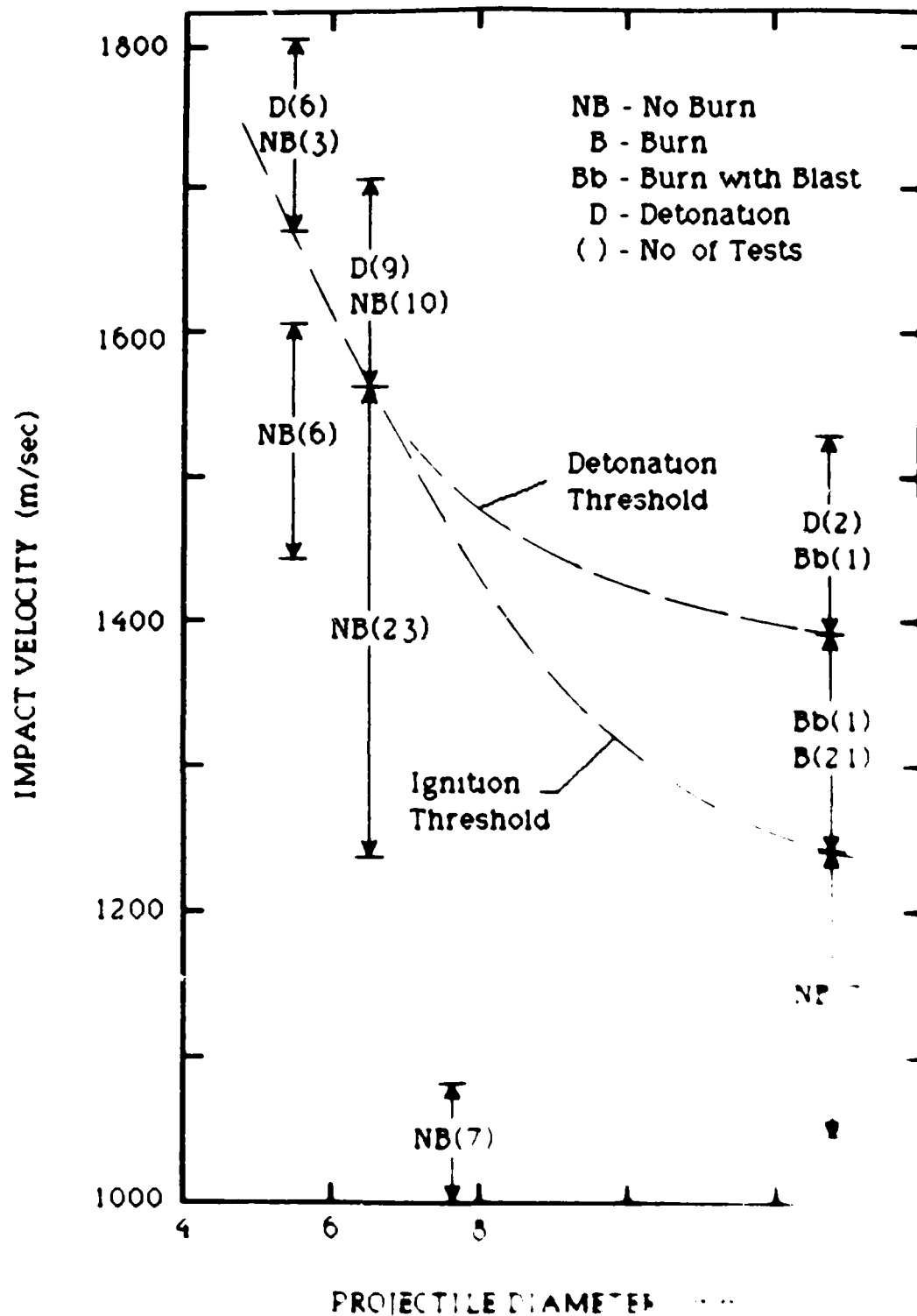


Figure 14. Impact ignition data.
(from Andersen and Moore, 1974)

Other systems which may model elements of hot spots in detonation of composite energetic materials have also been studied. These include detonations in fuel sprays in air and in media with layered equivalence ratio distributions. Such studies should be reviewed to ascertain relevant concepts for solid energetic materials.

CHAPTER IV. NEAR AND FAR TERM TECHNOLOGY NEEDS

Having established test methodology and deficiencies in understanding resulting from current practice, in this chapter technology needs are identified and presented for each area and followed by more general, longer range needs common to many of the technical areas.

A. Near Term Needs by Technology Area

1. Critical Diameter; 2. Shock to Detonation Transition

The technology needs for these two areas are addressed in this combined section. The problem of determining the critical diameter of a particular formulation is essentially a limited shock to detonation (SDT) study.

Near Term - Predicting solid rocket motor response to shock inputs

A mature detonation science, able to fundamentally describe and model equations of state and their relationship to chemical reactions taking place across the detonation reaction zone, is many years away. In the interim, experimentally supported modeling studies will continue to provide the most useful information for those concerned with solid propellant shock sensitivity.

Predicting solid rocket motor response to shock is the most pressing SDT technology need for the solid propellant community. Engineering judgement,

based on small scale critical diameter and SDT testing, can't be relied upon to determine the real vulnerability of solid rocket motors to shock. Experimental programs are also extremely limited in terms of usefulness. The cost of just a few full-scale detonation tests on a typical missile stage is enormous. The expense of experimentally fully characterizing a motor with respect to different shock levels and shock loading rates is prohibitive.

A solid rocket motor should be as insensitive as possible to shock input. Making the rocket motor web thickness a little smaller than the propellant's critical diameter, so that detonation is unlikely, seems a good idea. Unfortunately, the various factors influencing the shock to detonation transition, such as confinement, initial temperature, and physical damage, can all individually substantially decrease the critical diameter of a particular propellant. Predicting the response of a motor to various shock stimuli, based on small scale tests, becomes an intractable problem.

A rational methodology to determine the true hazards of rocket motors is needed. The development of truly reliable rocket motor shock response modeling capabilities, based on an understanding of the interplay between confinement, critical diameter, physical damage, initial temperature, and small scale shock sensitivity, will satisfy the most crucial needs of organizations concerned with motor development.

Near Term - The development of a replacement for the standardized wedge test

The current test suffers from a number of deficiencies, in addition to its strengths, and the new test must address those deficiencies. It must be more economical to run in order to allow more complete parameterization studies to be performed within a reasonable cost budget. The new test needs to be more convenient and reliable in the handling of damaged samples, as well as provide adequate diagnostics, with run distance to detonation as a function of input pressure, as in the current wedge test, a minimum. Finally it needs to be as easily modeled as the wedge test is currently, and to allow comparison with the existing datum base. This latter requirement is not trivial as shown by the lack of successful efforts to model various gap test configurations, even after decades of use.

Near Term - Better characterization of test samples

Investigators should characterize and report the complete nature of the samples being tested. Thus, all parameters affecting sensitivity: damage, %TMD, chemical composition, temperature, particle size, etc., should be given. Very commonly U.S. samples of RDX contain HMX as an impurity (and vice versa). This possibility is almost never reported in the literature, but hopefully it is considered. And it is also more appropriate to report the pressure in the sample than simply that at the end of a gap. This may be particularly important with samples showing a high degree of damage.

Longer Term - Comprehensive theory of Detonation

A comprehensive theory of detonation does not exist. The long term goal of future SDT work should be the development of a complete description of the detonation reactions occurring in condensed phase materials.

Future research will concentrate more and more on small-scale effects which contribute to the dynamics of detonation (Davis, 1987). Analytical models, using reactive fluid flow computations, are now sophisticated enough to account for much of the experimentally observed behavior of fully developed detonation waves. Experimental evidence shows that inhomogeneities (hot spots) due to density variations, temperature differences, or voids, have a very important influence on detonation propagation processes. No models exist which fully incorporate or account for microstructural influences on material response and decomposition chemistry during shock loading (Baer, 1986).

The continued development of detailed multiple phase reactive fluid flow models which account for the interactions of shock waves and explosive material at the detonation front is essential for a comprehensive theory of detonation. Such modeling requires very fast computers with large memory capacities; advances in modeling depend, to some extent, on the computing facilities available to detonation physicists.

Equally important to understanding SDT is the derivation of equations of state and decomposition mechanisms throughout the reaction zone of a detonating material. In recent years the use of laser spectroscopy has

greatly aided experimentalists and theoreticians in looking at the chemical phenomena associated with detonations over very short time spans.

The goal of a comprehensive theory of detonation is not unrealistic. The close association of modelers with the very active experimentalists who are probing the chemical kinetics of detonation processes promotes progress toward a useful theory. The wealth of experimental data promised as new techniques capable of much more precise measurements of the temperature, pressure, and spatial distribution of reaction products become more widely available will increase the opportunities for smaller organizations to contribute to the field of detonation physics, especially in the areas of modeling and chemical decomposition mechanisms.

3. Deflagration to Detonation Transition

Near Term - Improved experimentation

More complete pressure instrumentation is required on DDT tube experiments. The instrumentation should be able to span the pressure range from onset of reactions (ignition) to just before detonation. More complete spatial and temporal response is needed.

DDT tube tests need to be run on more realistic samples. While HMX powders and ball powder experiments provide understanding, they may not satisfactorily represent propellants or explosives.

Near Term - Modeling

Additional constitutive relations covering compaction, permeability, drag, and thermochemical reaction of various types of energetic materials are required. More realistic descriptions of the thermochemistry, particularly in the early stage reactions, should be used. The commonly used ignition criteria and simple pressure-dependent burn model should be replaced with a more complete description.

Longer Term - Instrumentation and effects of damage

Chemical species and temperature should be measured as functions of space and time, analogous to the short term need for pressure measurement.

The cause and extent of damage to various energetic materials must be clarified, as well as how the various types and extents of damage cause changes in DDT. To date most of the studies have been performed on idealized systems, not real, damaged propellants.

Efforts also need to be made to study DDT of freshly damaged energetic material. While in many laboratory experiments we study DDT of sample carefully prepared well in advance of the test, the real world situations have almost simultaneous damage and onset of reaction.

4. Delayed Detonation

Near Term - The development of an easy, reliable XDT test

Since XDT has been used to describe the behavior of materials under a variety of initiation conditions, it would be useful to study the behavior of a few, well characterized compounds under all conditions. It may be advisable to choose those conditions most favorable for subsequent analysis and modeling. Idealizations of the card gap and impact tests are possibilities. The result would hopefully be the criteria for a reliable XDT test procedure and parametric data to assist the longer term effort.

Longer Term - The prediction of XDT behavior from materials properties

A long term goal is the development of the capability to predict the delayed transition to detonation of an energetic material from the knowledge of the physical and chemical properties of the material. This will require knowledge of the micromechanics of material deformation and fracture, the chemical and physical properties of fractured surfaces, the ignition of energetic materials in response to high loadings, the spread and build-up of combustion waves in compacted media, and the subsequent transition of combustion waves into detonations. Many of these topics are common to DDT as well.

5. Thermal Response and Ignition

Near Term - Relating thermal initiation to hazard scenarios

Thermal initiation through various electromechanical inputs accounts for the bulk of accidents involving energetic materials. The correlation between impact, friction, and electrostatic initiation will ultimately depend on whether they can be related to the level and location of thermal energy generated. A detailed knowledge of energetic material thermal response thus becomes critical to understanding any hazardous initiation situation. Further research into the energy partitioning occurring during sensitivity testing should become synergistic. As the chemistry and physics of impact, friction, and ESD are applied to thermal initiation, an increased understanding of thermal effects will help our understanding of impact, friction, and ESD initiation.

Longer Term - Combustion chemistry (Baer, 1986)

Much uncertainty in the various tests for thermal stability and thermal ignition is the result of a lack of understanding of the chemistry of the various modes of combustion. Combustion physics of energetic materials require real-time measurement techniques that can identify important species and resolve reaction rates and thermodynamic paths in nano-second time scales. Optical diagnostic techniques developed for gas phase combustion studies can be adapted for condensed-phase materials. Advanced techniques are under development which can be used for both low and high temperature thermal decomposition kinetics.

6. Friction

Near Term - Standardized friction test

All of the methods discussed in Chapter II should be reviewed in order to select that one which is most easily modeled, i.e., for which the geometry of the sample and contact surfaces is most readily analyzed to extract the frictional energy input with time from thermal and/or impact loads to which the specimen is simultaneously exposed. Using this numerical model as a guide, predictions from the model should be compared against suitably placed instrumentation involving accelerometers and thermocouples or radiometers. The latter, gas sampling instrumentation, or both would also properly characterize the initiation event and time.

Longer Term - Compare sensitivities

Having established a suitable friction datum base as above, with parametric studies of the type discussed throughout the report, the model and measurements can then be cross-correlated with equally well-defined thermal and impact initiation data for the same energetic materials.

7. Impact

In view of the widespread usage of impact devices and the considerable amount of background and experience revealed in the questionnaire responses, it would seem that a renewed effort toward standardization and instrumentation of the impact test is needed. Some of the problems to be addressed are:

1. Reaction Detection - This should be straightforward in light of current instrumentation technology. What must be determined is the appropriate level and phenomena to be measured.
2. Instrumentation - Measurement of energy transmitted to the sample for initiation is preferred.
3. Parametric Studies - Control and independent variation of sample size, particle size, humidity, temperature, cure time, confinement, granulation, solid, and liquid should be accomplished.
4. Testing Procedure - Variables not accounted for in sample preparation would include test environment, impact surface maintenance, statistical methods and results evaluation.
5. Machine Design - If test device variability errors are to be eliminated from test results, standardization is imperative.

With respect to bullet and fragment impact, the following near term needs can be identified:

1. A test to rank explosives according to their shear sensitivity.
2. A parametric study to determine when shear effects are important compared to shock effects.

3. A study of burning under pressure to include an investigation of the cause of charge deconsolidation.

4. A study of the damage which occurs to an energetic material after projectile impact.

5. A means of ranking explosives for their susceptibility to multiple impact which uses mechanical property data or data from small scale tests.

8. Electrostatic Discharge

Near Term Technology Needs: Small Scale Test

A small scale ESD propellant sensitivity test needs to be developed which has at least the following attributes:

1. Small sample size. The utility of such a test is determined by factors such as sample cost and test safety. The sample must be large enough to allow for the prediction of the sensitivity of a full scale propellant from the results of the small scale test.

2. Indicate temperature effect on sensitivity - Since a prohibitively large number of samples would be required to determine the ESD threshold sensitivity as a function of temperature, the test must use a minimum number of samples required to result in a statistically reasonable sensitivity measurement at a minimum number of test temperatures.

3. Reflect full scale, fielded system sensitivity. The ESD hazard, as experienced during propulsion system transportation and deployment, should be reflected in the small scale test (is the sensitivity level for a charged object, e.g., a person, discharging to a propellant system the same as a charged propellant system discharging to a grounded object?). The fielded propellant system sensitivity may also be enhanced by its confinement. The test method should also reflect the effect of the time constant of the ESD discharge. It is well known (Mäki and Oy, 1977) that the propellant is a function of the RC time constant, i.e., the propellant sensitivity increases and then decreases with increasing time constant for a given energy.

Measure Electrical Properties

In order to characterize a propellant for ESD sensitivity, its electrical properties must be measured. Since the ESD event is transient in nature, the method of measurement of electrical properties needs to be specified. Some of the basic quantities which must be measured are resistivity, dielectric constant, and breakdown voltage or field strength. Some of the methods of measurement include:

1. Constant voltage, high resistance meter
2. Constant current electrometer
3. Alternating voltage, 1 KHz impedance bridge
4. Capacitive discharge, RC time constant

Since propellant is an electrically complex material, it needs to be determined which of these, or other, methods will provide the most accurate input for analytical models.

Longer Term Technology Needs

1. Develop an analytical model to predict the response of a propellant system from experimentally determined quantities. A satisfactory model would be capable of describing the buildup and dissipation of electrostatic charges in both small scale and large scale (including systems level) tests, based on measured electrical properties of the propellant and other components, and predicting and/or correlating the sensitivity of propellants to initiation by electrostatic discharge, based on the initiation sensitivity in suitable small scale tests.
2. Conduct basic research to understand the ESD phenomenon in energetic materials such as propellant.
3. Determine the effect (i.e. damage) of long term electric field application on propellant sensitivity.

B. General and Longer Term Requirements

In addition to the specific technology needs discussed in the previous section for the eight technical areas, there are general requirements which would improve the understanding and design practice for reducing hazards

associated with energetic materials. Included here are chemical kinetics, from overall multi-step ignition and burning rates to molecular level decomposition process studies. The mechanical and electrical properties need further characterization as well, as do transient ignition and combustion processes for solid propellants. Micromechanics research was another area recommended by most of the respondents to the questionnaire. Parametric studies are rarely available and should include method, stimulus level, and rate of initiation; propellant formation, geometry, confinement, age, initial temperature, and humidity are equally important. For applications to fielded systems, scaling procedures require clarification.

There were three other general areas for which near-unanimous interest was indicated: (1) the relation of ESD, friction, and impact tests to real-world scenarios; (2) the relationship between impact, friction, ESD, and thermal initiation; and (3) effects of damage, particularly on SDT, DDT, XDT, and critical diameter. Each of these topics will be discussed below; they have been recently addressed in more detail by Mellor et al. (1987).

Regarding the applicability of impact, friction and electrostatic test methodology to practical hazard situations (here as pertaining to fielded system threats, not manufacturing and processing scenarios), one difficulty is that frequently the true minimum ignition energy (the energy transferred to the sample prior to ignition, not that stored initially in the test device) is not measured and reported. Further confounding the interpretation of such data are the working definition of initiation or ignition, particularly when working with small samples, and the statistical analysis which is necessary to

characterize the results. An important parameter which should be varied is the rate of energy input to fully simulate practical threats (for example, to rely solely on SDT data to simulate high rate impact could be misleading since scenarios other than step inputs must be considered).

Remarkably little information is available on the equivalency of mechanical (impact and/or friction), electrical, and thermal initiation. Separation of frictional effects in impact tests is difficult, questions relating to energy transfer, conversion, absorption and dissipation and the generation of hot spots from different forms of input energy are unresolved, and events during the unloading process (e.g., chemical-mechanical interactions after impact) require considerable attention. However, until minimum ignition energies are measured, attempts to relate the quantitative information obtained in the four test procedures will not be meaningful. As a result preferred test methods are difficult to recommend.

Finally, it is the consensus that damage is an extremely important parameter for characterizing response severity, in that it augments the probability of detonation through increased surface area available for combustion. Here as well quantitative characterization of damage (and rehealing) is requisite for interpretation of the results (Boggs et al., 1985), but laboratory methods generally yield only percent of theoretical density. Apparently data from thermal and critical impact velocity tests where sample surface area to volume is varied have not been cross-correlated. Methods for creating realistic damage (as found during motor pressurization, for example) prior to testing are receiving limited study, as are models for fracture (Lee et al., 1984) and for combustion in pores and cracks.

CHAPTER V. LONG-RANGE PLAN ON HAZARDS

The EMHIAT activity was organized in late 1985, as noted in Chapter I. Responses to the questionnaire which is included as Appendix A were presented to EMHIAT by both the rocket propulsion industry and the DoE contractor laboratories in April of 1986. Three months later the DoD Joint Requirements Oversight Council issued definitions and criteria pertaining to Insensitive Munitions, which include devices containing solid propellants, for the three services (JROC, 1986).

Because these latter requirements were not available to the respondents as they prepared their briefings to EMHIAT, priorities established based on the April 1986 view are no longer current. Consequently, EMHIAT has reorganized those research and technology needs which result from the deficiencies cited in previous chapters into two categories, those pertaining directly to Insensitive Munitions and other, longer-term programs which are necessary to support the development of insensitive rocket and gun propellants and explosives. Related topics which EMHIAT considers important to the establishment of Insensitive Munitions conclude this chapter. We begin with a brief description of the Insensitive Munition Requirements.

A. Insensitive Munitions

A munition is a system or device which is "charged with explosives, propellants, pyrotechnics, [or] initiating compositions ... for use in connection with defense or offense, including demolition," and is considered

insensitive if it "will reliably fulfill ... performance, readiness, and operational requirements on demand, but will minimize the violence of a reaction and subsequent collateral damage when subjected to unplanned stimuli" (JROC, 1986). The tri-service-agreed tests used to meet the second definition are 1) fast cook-off, 2) bullet impact, for both of which no reaction more severe than burning (consumption of the energetic material and possible case rupture, but no fragments hazardous to personnel thrown more than 50 feet) is allowed, and 3) sympathetic detonation, for which no propagation from the initiated munition to others in the surroundings may occur. JROC (1986) indicates that additional future criteria may involve other tests such as slow cook-off, fragment impact, shaped charge jet, spall, electromagnetic pulse, and electrostatic discharge, if agreements on relevance and test procedures are forthcoming between the three services. Details of many of these systems-oriented tests may be found in either Weiss et al. (1984) or Taylor et al. (1985).

As has been stressed throughout the present report, EMHIAT has chosen to limit its attention to test procedures pertaining to energetic materials rather than systems which contain propellants or explosives. The plan which follows for research and technology requisite to meeting the goals for Insensitive Munitions should be viewed from this perspective.

B. Near Term Energetic Materials Research

By near term is meant those programs recommended by industry and DoE contractor laboratories which EMHIAT feels are directly related to the currently accepted tests for fast cook-off, bullet impact, and sympathetic detonation; the elements of the EMHIAT plan are organized accordingly.

1. Fast Cook-Off

Two respondent-identified programs apply to the fast cook-off scenario.

a. Improve chemical mechanisms and kinetics during thermal loading for prediction of thermal ignition

Much interest is expressed in developing better, more fundamental kinetic models. Experimental approaches discussed in Section IIE such as differential thermal analysis, differential scanning calorimetry, and accelerating rate calorimetry (Flanigan et al., 1986; Hermsen et al., 1986) have been suggested for use in determining kinetic parameters, but Boggs et al. (1975) have questioned the relevance of such data, and other kinetic data obtained at low pressure, low heating rates, and low reaction rates, to combustion, and perhaps to fast cook-off. For example, the thermolysis approach of Oyumi and Brill (1985) may be preferred. Landers (1986) points out in addition that the first two methods and thermogravimetric analysis use samples too small for extrapolation to composite propellants and that accelerating rate calorimetry has too low a sensitivity to be useful.

An equally substantial difficulty of these small-scale kinetic methods is their interpretation: energetic materials of interest can exhibit autocatalysis due to reactions in the crystalline solid state, depletion of a stabilizer, melting with decomposition, or true chemical autocatalysis in a homogeneous phase (Rogers, 1982; Flanigan et al., 1986). Donohue (1986) notes in addition that using these tests it is difficult to distinguish the volatilization, pyrolysis, and oxidation steps, for which the individual kinetics, reaction intermediates, and products are generally unknown.

More sophisticated diagnostics, such as emission spectroscopy and laser induced fluorescence in the gas phase or single-pulse Raman scattering for reaction intermediates and products (Baer, 1986; Delpuch et al., 1981; Parr and Hanson, 1986), X-ray photoelectron spectroscopy, thin layer chromatography or chemical ionization mass spectroscopy for surfaces or the solid phase (Sharma et al., 1985), and flash X-ray absorption (Lee et al., 1984) to characterize the mechanical state will yield further insight.

b. Perform molecular level decomposition studies for insensitive energetic materials

Theoretical work at the molecular level can identify molecular configurations which exhibit decreased sensitivity.

2. Bullet Impact and Sympathetic Detonation

Six programs suggested by industry and the DoE contractor laboratories are relevant to both bullet impact and sympathetic detonation.

a. Develop improved experimental methods to create and characterize damage and characterize rehealing

It is the consensus that damage is an extremely important parameter which determines initiation ease and response severity. The two key problems in this area are how to create and then how to measure the extent of damage. As early as the mid-1960's Elwell et al. (1967) for Project SOPHY recognized the importance of "defective" material and endeavored to make specimens with

both unconnected pores of varying diameters and total porosity, and connected voids in various ranges of specific surface area.

Damage of the first type of 5 to 13 percent was obtained by mechanical means and up to 23 percent via additives which vaporized during curing. Samples cast on honeycombs, then cycled from ambient to liquid nitrogen temperatures three times, generated connected voids. Characterization was accomplished through optical microscopy for pore diameter, toluene adsorption for specific surface area, and density comparisons of samples in air and in oil for pore volume.

In a closely related area, the shotgun-critical impact velocity test for DDT (see Section C1 of Chapter II) is of particular concern because the shear breakup is different from that expected in motor scenarios (Flanigan et al., 1986; Hermesen et al., 1986; Landers, 1986).

b. Measure mechanical properties for energetic materials

In SDT and other forms of mechanical initiation, stress-strain measurements at appropriate pressures, temperatures, and applied loading rates are needed. Other properties such as bulk modulus (or Poisson's ratio), stress relaxation modulus, and so forth may be useful as well for understanding, correlating, or modeling.

If such measurements are made independently, then they will enjoy more confidence: sensitivity to shock, or ease of SDT, could then perhaps be correlated with the mechanical properties (Baer, 1986; Barnes, 1986) instead

of deduced from comparisons of SDT hydrocode calculations with experiments. Both the undamaged and damaged heterogeneous material should receive attention (Hermesen et al., 1986; Baer, 1986). Other important parametric variations should include formulation (e.g., binder type, oxidizer type and size distribution), age, and ambient humidity.

c. Improve chemical mechanisms and kinetics during shock loading for prediction of detonation (SDT and DDT)

The major deficiency with hydrocodes, especially for some propellant applications, is the absence of descriptions of chemical energy release rates. Most of these codes assume infinitely fast chemical kinetics; that is, the material is unreacted or fully reacted. For many applications where induction and reaction zones are small (e.g., high explosives and some very high energy propellants), these assumptions are tolerable.

Attempts at including a chemical energy rate dependence in some hydrocodes have used a pressure dependent rate analogous to the burn rate of solid propellants, as opposed to the more traditional Arrhenius dependence on reaction temperature. Examples include the Forest Fire code (Mader and Forest, 1976) and more advanced models (see for example Lee et al., 1984; Moulard et al., 1985) which some in the explosives community (Rabie, 1986) do not consider as correlations, but rather "sophisticated" determinations of a "satisfactory state dependence for the reaction rate." In more recent work Tang et al. (1985) note that the Forest Fire model is an attempt to describe heat transfer from initiated reaction sites via conduction and turbulent transport, which for SDT are assumed rate-limiting, i.e., much slower than the appropriate kinetics.

Others criticize these models as empirical and inadequate for non-SDT calculations (Flanigan et al., 1986; Hermsen et al., 1986), noting that parameter adjustments are required to fit SDT data for different materials (Moulard et al., 1985; Baer, 1986). The hydrocodes using such models are also unable to predict initiation to a deflagration instead of detonation. In addition, particularly for large rocket motors, the critical diameter cannot be predicted as a function of formulation of the energetic material, or of the size distribution of the embedded oxidizer particles (Hermsen et al., 1986; Moulard et al., 1985). Consequently much interest was expressed in developing better, more fundamental kinetic models (some hydrocodes now use global Arrhenius expressions with or without Forest Fire; see Mader and Kershner, 1985). The study of reaction zone dynamics at full detonation for insensitive energetic materials is particularly relevant.

There is a broad range of requirements for kinetic parameters, from global pre-exponential factors and activation energies obtained in small-scale tests (Landers, 1986) or via critical diameter interpretation with a suitable hydrocode (Hermsen et al., 1986), to mechanisms for fast versus slow kinetics and studies which reveal "microstructural influences on decomposition chemistry" (Baer, 1986). It is also argued that more meaningful research would couple thermomechanical and kinetic analyses to elucidate mechanical response after initiation (Baer, 1986; Lee, 1986).

d. Study deflagration of energetic materials at high pressure as applicable to DDT

In a global sense, energy is transferred at higher rates at high pressure, which could then lead to either fracture followed by reaction or reaction followed by product gas release resulting in fracture. Since damage of the material is intimately involved in DDT in order to generate large surface areas for combustion (Bernecker, 1984), studies of combustion in pores, cracks, and other defects are also important (Bradley and Boggs, 1978; Butler and Krier, 1984; Baer, 1986; Kuo and Moreci, 1986).

e. Improve chemical mechanisms and kinetics for prediction of long term thermal runaway in large scale (bullet impact only)

Many of the comments made in Section 1 above under paragraphs a and b are appropriate.

f. Perform time and space-resolved measurements in SDT with parametric variations (formulation variables, geometry, age, damage, initial temperature and humidity, and confinement) and various input wave types (shock, ramp, shock plus reloading, shock plus unloading, transverse shear). Document XDT observations

Since sensitivity to shock is also affected by the shape of the input wave with time (see for example Setchell (1981) and Andreev et al. (1985)), the rate of energy input, and unloading and reloading histories should also be varied to fully simulate practical threats (scenarios other than step inputs must be considered) and develop increased understanding (Flanigan et al., 1986; Baer, 1986).

The various mechanisms proposed for hot spot formation (see discussion in Francis and Hufferd, 1986, Kim and Sohn, 1985, Taylor, 1985, Coffey, 1985, and Anderson, 1981 and their additional earlier citations) are controversial and should be clarified (Hermsen et al., 1986; Rabie, 1986; Baer, 1986; Donohue, 1986). Various pore collapse models are popular (Frey, 1984, 1985; Andersen and Gillespie, 1980), since they require initial material porosities on the order of only one percent (Kim and Sohn, 1985; Kim, 1986), but equally debatable.

Rabie (1986) notes that hydrocodes for SDT are moving from homogeneous to hot spot approaches, as reported for example by Tang et al. (1985), but that "detailed dynamics of 'hot spots' of any kind have never been measured." He recommends time-resolved optical multicolor pyrometry on a hot spot coupled with finite element calculations for the experiment so that the relevance of hot spots, shear bands, viscous work and so forth can be studied. Coffey and DeVost (1986) have reported preliminary infrared measurements of hot spots in energetic and inert crystals impacted in drop weight machines.

In a related vein, Baer (1986) feels the next logical step in DDT experiments is obtaining time and space resolved measurements of pressure, for example.

C. Small-scale Formulation Screening Tests

Industry's suspicion, discussed briefly in the summary section of Chapter III, is that the routinely run small-scale laboratory test results for thermal, friction, impact, and ESD initiation cannot be meaningfully used to

screen pint-sized batches of candidate formulations, to prevent accidents during processing, or to design insensitive munitions for the field. In the processing area, Napadensky et al. (1978) provide an excellent review of then-current tests of this type and their relation to various steps in manufacturing, as well as selected accident data obtained from the DoD Explosives Safety Board.

In general comments on existing traditional hazard test methodology, Landers (1986) wonders if results of a given test could be predicted assuming the fundamental ignition mechanisms were understood. Rabie (1986) voices a similar concern. Coupled modeling and test refinement (or development) are required, as in the nearly-infinite-confinement (1500 atm or less) thermal reactor used at Livermore (Tarver et al., 1979; McGuire and Tarver, 1981; Lee, 1986). Since the heat transfer in this device can be calculated, it provides a fixture for comparison of various kinetic models with measured times to explosion. Modeling of ESD, impact, and friction tests would similarly improve their applicability to non-laboratory situations as well as provide guidance into preferred test hardware for improved sensitivity characterization.

1. Electrostatic Discharge

There is an urgent need to clarify and understand mechanisms of ESD ignition of energetic materials (Hermesen et al., 1986; Donohue, 1986; Rabie, 1986; DeButts et al., 1986; Landers 1986) since the Pershing II accident (Anon., 1985a). JROC (1986) has designated ESD as a possible future Insensitive Munitions criterion as well. Standard capacitive discharge tests

show the PII propellant to be one of the safest available from Hercules (DeButts et al., 1986). Hermesen et al. (1986) noted that the same test places all their cured propellants in the insensitive category, so that hazards predictions are impossible, and that the larger-scale French test does not improve the situation meaningfully. They also observe up to ten kilovolts during processing and handling operations in the plant, but are unable to determine the risk represented. Determination of the various electrical properties and refinement of ESD test procedures will both lead to improved discrimination between propellants.

- a. Generate and use a model to define and design a small-scale ESD test.
- b. Construct small-scale ESD test, including instrumentation to measure energy as a function of time to the sample, and optimize test to measure minimum ESD ignition energy
- c. Perform parametric studies for various energetic materials of interest to characterize minimum ESD ignition energies. Vary formulation variables (some to include catocene or ferrocenes), initial temperature, damage, confinement, ambient humidity, age, and so forth
- d. Measure electrical properties (volume resistivity, surface resistivity, dielectric constant, breakdown potential) for energetic materials and parametric variations in c above

The goal of these four programs is to develop a model, from basic principles or empirically, to predict the response of solid propellant to an

electrostatic discharge stimulus. The methodology to obtain the basic electrical properties of resistivity, dielectric constant, and breakdown voltage of propellants will be required since these quantities will be necessary as input to the model. The model will be used to define and design a laboratory scale test for screening ingredients and new formulation propellants for ESD sensitivity. A second test is desired to predict the ESD sensitivity of full scale propellant systems using a minimum size sample. Both tests will be instrumented to determine the minimum ESD ignition energy. The parametric variables identified to be of particular interest both in ESD and the impact and friction studies to be discussed below are (Flanigan et al., 1986; Hermesen et al., 1986; Landers, 1986): formulation variables, particularly oxidizer concentration (or solids loading) and oxidizer particle size distribution; initial temperature and temperature history; confinement; ambient humidity; initiation energy as a function of time; age of the specimen; and fresh and stale damage.

2. Impact and Friction

In addition to serving as screening methods for small energetic material samples, traditional impact and friction tests discussed in Sections F and G of Chapter II can also be thought of as relatively inexpensive procedures to study initiation during mechanical deformation. The mechanical property measurements itemized above under Bullet Impact and Sympathetic Detonation should be conducted in conjunction with the following programs as well.

a,b. Model to understand, refine, and instrument small-scale impact (friction) test to measure energy as a function of time to the sample

c,d. Perform parametric studies for various energetic materials of interest to characterize minimum impact (friction) initiation energies. Vary formulation variables (some to include catocene or ferrocenes), initial temperature, damage, confinement, ambient humidity, age, and so forth

In the traditional laboratory impact and friction (and ESD) tests the interpretation of initiation or ignition, particularly when using small samples on the order of milligrams, is confounded by the qualitative working definition of a positive event (a flash, pop, or odor noted by the operator). Sometimes it is required that the sample be consumed completely during the test. Landers (1986) recommends that the tests be standardized to define ignition in terms of the detection of products of decomposition or combustion, which could be accomplished via infrared absorption or gas sampling with a specific threshold for initiation (so many parts per million per milligram of sample) selected through the above experimental programs.

Another major difficulty is that frequently the energy transferred to the sample prior to ignition is not monitored (Flanigan et al., 1986; Hermesen et al., 1986; Landers, 1986; Donohue, 1986; Barnes, 1986). Specifically, the rate of mechanical energy input must be varied and measured to yield, for friction, either energy per unit area and time at ignition (Flanigan et al., 1986) or speed/normal force curves for ignition which could be related explicitly to handling and machining operations (Hermesen et al., 1986). For impact, the work of Coffey et al. (1986) with an instrumented drop weight machine or shotgun launched impactor, in both of which the fraction of total delivered energy required to plastically deform and ignite the specimen is obtained and reported as critical initiation energy, is of special interest (Hermesen et al., 1986).

Finally, the use of calculations for these tests to distinguish overall and local inputs and to guide additional instrumentation needs and test methodology improvements is essential.

D. Elements of the Plan which are Underway in DoD Laboratories

The two cook-off related programs described in Section B are oriented toward chemical kinetics and mechanisms both fundamental and more global. Advanced experimental methods and diagnostics, as well as theoretical work are required. A recent workshop (Husk, 1987) reviews some relevant current work in the various DoD agencies.

The various research suggestions itemized in Section B.2, Bullet Impact and Sympathetic Detonation, are concerned with damage characterization, mechanical properties, chemistry during both shock loading and slow thermal runaway, and more broadly based SDT studies. Some of this work is appropriate to the recently issued ONR Accelerated Research Initiative entitled "Crystal Structure Decomposition."

In the mechanical property category low dynamic rate uniaxial tests, which are usually conducted, are to be supplemented with data under triaxial loading and at high rates of strain. In many energetic materials, pressure and strain rate will have a major effect on flow stress, and this in turn affects hot spot formation and ignition. How and when fracture and breakup occur are required inputs as well.

Current DoD laboratory studies on SDT may be found in Liddiard and Forbes (1987), Graham et al. (1987), and Boyer and Mallory (1987).

Another program concerns deflagration at high pressures. Although some work is in progress to measure burning rates (see Velicky and Voight, 1985), more effort is required. Furthermore, there is a need to understand why some materials deconsolidate during burning under pressure (e.g., on the order of 1500 psia for Comp B) and thus burn violently, while others do not deconsolidate and exhibit slower combustion.

Although utilization of standard or modified small-scale formulation screening tests continues (see Yee, 1987a,b for impact) the major point of the programs listed in Section C above is the vital, parallel inclusion of fundamental modeling of the test in order to clarify and refine or replace the traditional methods for ESD, friction, and impact. Better instrumentation and broader parametric studies are also called for. Some work of this type is ongoing (CPIA, 1987 for ESD; Coffey et al., 1986 for impact).

The general conclusion is however that very few of the specific elements in the Long-range Plan on Hazards, assembled from industry and DoE contractor laboratory suggestions, are underway at or contracted by the various Army, Navy, and Air Force organizations at the present time.

E. Omissions from the Plan Relevant to Insensitive Munitions Criteria

During EMHIAT's discussion of the Long-range Plan enumerated in Sections B and C above, other research needs not addressed by the Plan became apparent

as resources are focussed upon the Insensitive Munitions goals (JROC, 1986). We conclude with a brief discussion of these additional areas identified by EMHIAT.

There is a need to understand the mechanics which lead to sympathetic detonation in large arrays of munitions. A few years ago, many people felt that sympathetic detonation is a special case of shock initiation, but a number of results demonstrate that other things occur. They are undoubtedly related to crushing, XDT, and DDT, but the interrelationships are not clear. Most importantly, we need to know which small scale tests will tell us if a problem is likely to occur in large scale array tests.

Regarding bullet impact, models for terminal ballistics and penetration dynamics are inadequate, and definition of a procedure to simulate multiple bullet or fragment impacts, in such a way that understanding of the process is obtained, is difficult.

We need to understand what controls the violence or severity of reaction under cookoff conditions. Some qualitative information is available, which indicates that the brittleness of the material and the nature of the low temperature decomposition are important. However, there is no known way to use the results of small-scale tests to predict the severity in a cookoff test. As noted previously, chemical and degassing effects, as well as thermal expansion particularly at slow rates in large scale, obscure our ability to extrapolate.

Since most existing hazard tests are not or cannot be modeled, it follows that changes in scale must be accompanied by additional testing, which is very expensive. In addition, if the initiation mechanism is unknown based on years of work with traditional small-scale test methods, limited for all practical purposes to providing relative rankings, how can one extend these results with any confidence to larger sizes? Thus modeling is strongly urged throughout EMHIAT's Long-range Plan presented in this Chapter.

Because the formulation screening tests are inadequate to identify insensitive energetic materials, and larger scale threats and tests are even more poorly defined on a fundamental basis, it must be concluded that the criteria for Insensitive Munitions set by JROC (1986) are indeed ambitious. EMHIAT strongly urges its programs comprising the Long-range Plan be funded in order to assist in this important effort.

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APPENDIX A. COVER LETTER AND
ENERGETIC MATERIAL HAZARD INITIATION
TECHNOLOGY ASSESSMENT



DEPARTMENT OF THE ARMY
UNITED STATES ARMY MISSILE COMMAND
REDSTONE ARSENAL, ALABAMA 35898

Dear Mr. XXXXXX:

The Department of Defense is emphasizing the reduction of hazards associated with solid propellants. A Tri-Service team has been established to assess current hazard technology and to develop a research plan to correct deficiencies identified in the assessment. This Tri-Service group is called the Energetic Material Hazard Initiation Assessment Team (EMHIAT).

The assessment process begins by EMHIAT asking the industrial contractors and government laboratories to describe their current hazard characterization methods, both experimental and analytical, and to cite the deficiencies in these practices. This query will be done using the questionnaire (enclosure 1) and by briefings, of up to 1/2 day duration, by the contractors to EMHIAT. These briefings are tentatively scheduled for the week of 21 April 1986. EMHIAT will then assess this information obtained via the questionnaire and briefings and develop the DoD Long-Range Research and Technology Plan for Hazards.

The output of this group will consist of:

- o a written assessment of current methods and practices;
- o a written identification of deficiencies in current practices;
- o a Long-Range Research and Technology (5.1 and 6.2) Plan for correcting these deficiencies;
- o briefings on the assessment of current methods, identification of deficiencies and Long-Range Plan to personnel from academia, industrial contractors, and government laboratories having the skills necessary to contribute in this effort.

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Seven companies - Aerojet; Atlantic Research Corporation; United Technologies-Chemical Systems Division; Hercules, Inc; Morton Thiokol; Rocketdyne; and Talley Industries - are requested to participate in this effort. You have been identified by EMHIAT as the focal point for your organization; however, we would appreciate a response from both your technical and safety personnel. Department of Defense representation will include the Air Force Office of Scientific Research, Air Force Rocket Propulsion Laboratory, Army Research Office, Army Armament Research and Development Center, Army Ballistic Research Laboratory, US Army Missile Command, Office of Naval Research, Office of Naval Technology, the Naval Surface Weapons Center and the Naval Weapons Center. In addition, the questionnaire will be sent to Lawrence Livermore National Laboratory, Los Alamos National Laboratory and Sandia Laboratories.

EMHIAT members, affiliations and phone numbers are provided as enclosure 2. The team is chaired by Dr. A. M. (Mac) Mellor of the U.S. Army Research Office.

While the assessment is to be an open forum, EMHIAT will respect the proprietary nature of contractor input (as identified). The assessment report will be in the form of a generalized overview.

This effort is fully consistent with the goals and efforts of the Joint Army-Navy, NASA-Air Force (JANNAF) Propulsion Systems Hazard Subcommittee.

We hope you will find this Technology Assessment activity a worth-while opportunity to interact closely with our Energetic Material Hazard Initiation Assessment Team. Not only will it provide a new infusion of ideas into our planning but it will also provide you with an opportunity to guide our programs toward those areas you feel will result in the greatest payoff in the field of energetic material hazard initiation. We sincerely hope that your organization will participate. If you have any questions, please contact any team member.

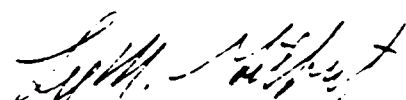
Sincerely,



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2 Enclosures

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ENERGETIC MATERIAL HAZARD INITIATION TECHNOLOGY ASSESSMENT



**Department of Defense
Energetic Material Hazard
Initiation Assessment Team**

February 1986

Because of increased emphasis within the Department of Defense on propellant hazard initiation we are embarking on the following Technology Assessment. The questions raised are intended to establish design techniques and tests used, their level of technology, and the accuracy and adequacy of these tests/techniques. The information provided in response will aid in the identification of those design technology areas which most need improvement.

Future technology will be guided by the results of current research efforts to meet the needs and desires of the designer. Some of the questions will be used to determine which technologies are most needed or have the greatest promise of improving design in order to develop a framework for the programming of technology development efforts.

Both near-term and long-term technologies are important in this assessment. Near-term efforts can usually be defined in terms of extending or improving current technology or practice by well-defined (scope, cost, and manpower) efforts. Longer term efforts can generally be defined in terms of the desired capability for which there is little or no developed or postulated technology; consequently, the means of achieving their advantages are less well-defined.

Questions posed in this questionnaire are not all-inclusive. They represent DoD perceptions of current problem areas which are provided as guides to industry to stimulate the definition of needs. Responses will be used to establish priorities for future programs. Proposals for technology development are not, however, being sought. While costs, times, and risks may be considered, the information being sought should be a statement of the technology need which identifies the shortcoming or deficiency being addressed. A technical approach may be provided if one is identifiable.

The hazard threats relevant to the questionnaire include sympathetic detonation, fragment/bullet impact, fast and slow cookoff, inadvertent ignition, dropping/crushing, and shaped charge impact. The technology areas related to these system needs include critical diameter, DDT, SDT, XDT, thermal response and ignition, friction, impact, and electrostatic discharge (ESD). The condition of the energetic material sample with respect to each of these technology areas is clearly important; included in this latter category are formulation, geometry, age/damage, initial temperature and humidity, confinement, and method of initiation. In responding to the questions concerning current practice and technology needs in each technology area below, keep in mind how the initial propellant and test conditions affect the answers to the questions.

The organization of the questionnaire is an eight by four by three matrix of technology areas, concerns, and questions.

Eight Technology Areas

1. Critical Diameter
2. DDT
3. SDT
4. XDT
5. Thermal Response and Ignition
6. Friction
7. Impact
8. ESD

Four Concerns

1. Small Scale Tests
2. Large Scale Tests
3. Physical/chemical Mechanistic Understanding
4. Comments?

Three Questions (Each to be answered in terms of propellant [a] formulation, [b] geometry, [c] method of initiation, [d] age/damage, [e] initial temperature and humidity, and [f] confinement)

1. What is your company's current practice?
2. What are the deficiencies in this practice?
3. What basic and applied research would mitigate or alleviate the hazard?

Obviously, the responses to the questionnaire could be voluminous. Therefore, your responses should be limited to synopses of points of information which need to be transmitted. If graphs, charts, or tables would be beneficial to the discussion, such additions are welcome.

I. In the technical area of shock-to-detonation transition (SDT).

A. Small scale SDT test methods and results.

1. What are your company's current test methods (test configuration, sample size, types of formulations, age, confinement, method of initiation), what type of results do you achieve, and how do you use these results?
2. What are the deficiencies in small scale tests, resulting data, and application of these data?
3. How might basic and applied research help overcome these deficiencies?

B. Large scale SDT test methods and results.

1. What are your company's current test methods (test configuration, sample size, types of formulations, age, confinement, method of initiation), what type of results do you achieve, and how do you use these results?
2. What are the deficiencies in large scale tests, resulting data, and application of these data?
3. How might basic and applied research help overcome these deficiencies?

C. Physical/chemical mechanistic understanding of SDT.

1. In your company, what is the current level of physical/chemical mechanistic understanding of SDT? (E.g., largely empirical correlation, first principles modeling, etc.)
2. What are the deficiencies in mechanistic understanding?
3. What basic and applied research might help overcome these deficiencies?

D. Anything else that you would like to add concerning SDT: e.g., have you looked at other considerations (parametric studies of propellant formulations, sample geometry, age, damage, initial sample temperature, humidity, confinement) with respect to SDT?

II. Critical diameter determination.

A. Critical diameter test methods and results.

1. Does your company currently measure the critical diameter of propellants and, if so, what are your current test methods (include test configuration, sample size, sample size, sample formulations or types of formulation, age, confinement, method

of initiation)? What type of results do you achieve, and how do you use these results?

2. What are the deficiencies in critical diameter tests, resulting data, and application of data? Do you compare critical diameter data to motor size, and/or do you test shock sensitivity of motors and compare to critical diameter?
3. How might basic and applied research help overcome these deficiencies?

B. Physical/chemical mechanistic understanding of critical diameter.

1. In your company, what is the current level of physical/chemical mechanistic understanding of critical diameter (e.g., largely empirical correlation, first principles modeling, etc.)?
2. What are the deficiencies in mechanistic understanding?
3. What basic and applied research might help overcome these deficiencies?

C. Anything else that you would like to add concerning critical diameter, e.g., have you parametrically studied other considerations (parametric studies of propellant formulation, sample geometry, age, damage, initial sample temperature, humidity, confinement) with respect to critical diameter?

III. Deflagration-to-detonation transition (DDT).

A. Small scale DDT test methods and results.

1. What are your company's current test methods (test configuration, sample size, types of formulation, age, confinement, method of initiation), what type of results do you achieve, and how do you use these results?
2. What are the deficiencies in small scale tests, resulting data, and application of these data?
3. How might basic and applied research help overcome these deficiencies?

B. Large scale DDT test methods and results.

1. What are your company's current test methods (test configuration, sample size, types of formulations, age, confinement, method of initiation), what type of results do you achieve, and how do you use these results?
2. What are the deficiencies in large scale tests, resulting data, and application of these data?

3. How might basic and applied research help overcome these deficiencies?

C. Physical/chemical mechanistic understanding of DDT.

1. In your company, what is the current level of physical/chemical mechanistic understanding of DDT? (E.g., largely empirical correlation, first principles modeling, etc.)
2. What are the deficiencies in mechanistic understanding?
3. What basic and applied research might help overcome these deficiencies?

- D. Anything else that you would like to add concerning DDT: e.g., have you looked at other considerations (parametric studies of propellant formulations, sample geometry, age, damage, initial sample temperature, humidity, confinement) with respect to DDT?

IV. Delayed detonation (XDT).

A. Small scale XDT test methods and results.

1. What are your company's current test methods (test configuration, sample size, types of formulations, age, confinement, method of initiation), what type of results do you achieve, and how do you use these results?
2. What are the deficiencies in small scale tests (test configuration, sample size, types of formulations, age, confinement, method of initiation), resulting data, and application of these data?
3. How might basic and applied research help overcome these deficiencies?

B. Large scale XDT test methods and results.

1. What are your company's current test methods, what type of results do you achieve, and how do you use these results?
2. What are the deficiencies in large scale tests, resulting data, and application of these data?
3. How might basic and applied research help overcome these deficiencies?

C. Physical/chemical mechanistic understanding of XDT.

1. In your company, what is the current level of physical/chemical mechanistic understanding of XDT? (E.g., largely empirical correlation, first principles modeling, etc.)

2. What are the deficiencies in mechanistic understanding?
 3. What basic and applied research might help overcome these deficiencies?
- D. Anything else that you would like to add concerning XDT: e.g., have you looked at other considerations (parametric studies of propellant formulations, sample geometry, age, damage, initial sample temperature, humidity, confinement) with respect to XDT?

V. Thermal response and ignition.

A. Small scale thermal response and ignition test methods and results.

1. What are your company's current test methods (test configuration, sample size, types of formulations, age, confinement, method of initiation), what type of results do you achieve, and how do you use these results?
2. What are the deficiencies in small scale tests, resulting data, and application of these data?
3. How might basic and applied research help overcome these deficiencies?

B. Large scale thermal response and ignition test methods and results.

1. What are your company's current test methods (test configuration, sample size, types of formulations, age, confinement, method of initiation), what type of results do you achieve, and how do you use these results?
2. What are the deficiencies in large scale tests, resulting data, and application of these data?
3. How might basic and applied research help overcome these deficiencies?

C. Physical/chemical mechanistic understanding of thermal response and ignition.

1. In your company, what is the current level of physical/chemical mechanistic understanding of thermal response and ignition? (E.g., largely empirical correlation, first principles modeling, etc.)
2. What are the deficiencies in mechanistic understanding?
3. What basic and applied research might help overcome these deficiencies?

D. Anything else that you would like to add concerning thermal response and ignition: e.g., have you looked at other considerations

(parametric studies of propellant formulations, sample geometry, age, damage, initial sample temperature, humidity, confinement) with respect to thermal response and ignition?

VI. Friction.

A. Small scale friction test methods and results.

1. What are your company's current test methods (test configuration, sample size, types of formulations, age, confinement, method of initiation), what type of results do you achieve, and how do you use these results?
2. What are the deficiencies in small scale tests, resulting data, and application of these data?
3. How might basic and applied research help overcome these deficiencies?

B. Large scale friction test methods and results.

1. What are your company's current test methods (test configuration, sample size, types of formulations, age, confinement, method of initiation), what type of results do you achieve, and how do you use these results?
2. What are the deficiencies in large scale tests, resulting data, and application of these data?
3. How might basic and applied research help overcome these deficiencies?

C. Physical/chemical mechanistic understanding of friction.

1. In your company, what is the current level of physical/chemical mechanistic understanding of friction? (E.g., largely empirical correlation, first principles modeling, etc.)
2. What are the deficiencies in mechanistic understanding?
3. What basic and applied research might help overcome these deficiencies?

D. Anything else that you would like to add concerning friction: e.g., have you looked at other considerations (parametric studies of propellant formulations, sample geometry, age, damage, initial sample temperature, humidity, confinement) with respect to friction?

VII. Impact.

A. Small scale impact test methods and results.

1. What are your company's current test methods (test configuration, sample size, types of formulations, age, confinement, method of initiation), what type of results do you achieve, and how do you use these results?
2. What are the deficiencies in small scale tests, resulting data, and application of these data?
3. How might basic and applied research help overcome these deficiencies?

B. Large scale impact test methods and results.

1. What are your company's current test methods, what type of results do you achieve, and how do you use these results?
2. What are the deficiencies in large scale tests, resulting data, and application of these data?
3. How might basic and applied research help overcome these deficiencies?

C. Physical/chemical mechanistic understanding of impact.

1. In your company, what is the current level of physical/chemical mechanistic understanding of impact? (E.g., largely empirical correlation, first principles modeling, etc.)
2. What are the deficiencies in mechanistic understanding?
3. What basic and applied research might help overcome these deficiencies?

D. Anything else that you would like to add concerning impact: e.g., have you looked at other considerations (parametric studies of propellant formulations, sample geometry, age, damage, initial sample temperature, humidity, confinement) with respect to impact?

VIII. Electrostatic discharge (ESD).

A. Small scale ESD test methods and results.

1. What are your company's current test methods (test configuration, sample size, types of formulations, age, confinement, method of initiation), what type of results do you achieve, and how do you use these results?
2. What are the deficiencies in small scale tests, resulting data, and application of these data?
3. How might basic and applied research help overcome these deficiencies?

B. Large scale ESD test methods and results.

1. What are your company's current test methods (test configuration, sample size, types of formulations, age, confinement, method of initiation), what type of results do you achieve, and how do you use these results?
2. What are the deficiencies in large scale tests, resulting data, and application of these data?
3. How might basic and applied research help overcome these deficiencies?

C. Physical/chemical mechanistic understanding of ESD.

1. In your company, what is the current level of physical/chemical mechanistic understanding of ESD? (E.g., largely empirical correlation, first principles modeling, etc.)
2. What are the deficiencies in mechanistic understanding?
3. What basic and applied research might help overcome these deficiencies?

D. Anything else that you would like to add concerning ESD: e.g., have you looked at other considerations (parametric studies of propellant formulations, sample geometry, age, damage, initial sample temperature, humidity, confinement) with respect to ESD?

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) (U) The Army, Navy, and Air Force Energetic Materials Hazard Initiation Assessment Team (EMHIAT) was established in late 1985 to identify basic and applied research needs to mitigate hazards, particularly for solid rocket propellants, represented by unplanned initiation in manufacturing or handling fielded systems and during processing of energetic materials. The team has surveyed the solid rocket industry, the DoE contractor laboratories, and DoD efforts related to explosives, gun, and rocket propellants. Findings of the survey and a Long-range Plan for Hazards are summarized in the present report. (U) In July 1986 the DoD Joint Requirements Oversight Council issued criteria for Insensitive Munitions, all of which contain energetic materials. EMHIAT strongly recommends the Plan documented here as essential to meeting these criteria in a cost effective and timely manner.					
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Block 18 (continued):

detonation, thermal response and ignition, impact, friction, electrostatic discharge, insensitive munitions, cook-off, bullet/fragment impact, sympathetic detonation.